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A Modified Route to Cyclopenta[C]Thophenes Via Grignard Reagents

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A MODIFIED ROUTE TO CYLCYOPENTA[*C*]THIOPHENES VIA GRIGNARD REAGENTS

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A MODIFIED ROUTE TO CYLCYOPENTA[*C*]THIOPHENES
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A MODIFIED ROUTE TO CYCLOPENTA[*C*]THIOPHENES

VIA GRIGNARD CHEMISTRY

Amber J. Bell December 2007 56 pages

Directed by: Dr. Chad A. Snyder

Department of Chemistry Western Kentucky University

The synthesis of cyclopenta[*c*]thiophenes is sparsely found in literature due to the several difficulties of their synthesis. Our research has shown that we could modify a previously known route to 1,3-disubstituted cyclopenta[*c*]thiophenes using traditional Grignard chemistry. Along the way we discovered the synthetic route we were using had several omissions. Therefore, we were required to completely fill in missing experimentals in order to obtain each cyclopenta[*c*]thiophene intermediate, in high purity and good yield. In addition, we were able to fully characterize via NMR, our intermediates which was found in the literature. Finally, we were able to show using ^{1}H and ^{13}C NMR spectroscopy evidence of 5-alkyl-1,3-disubstituted cyclopenta[*c*]thiophenes by treating 1,3-dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thio-phene-5-one with an alkyl Grignard reagent.

A series of cyclopenta[*c*]thiophene intermediates will be presented along with their ^{1}H and ^{13}C NMR spectra. A discussion of cyclopenta[*c*]thiophene synthesis will be provided along with attempts to improve its experimental conditions. A paper has been submitted to *Letters in Organic Chemistry* to report our work.

I. ORGANIC POLYMER CONDUCTIVITY AND BACKGROUND

Organic Conductors. All materials can be classified into the three categories of conductor, semiconductor, and insulator. These categories depend on the materials electrical properties. In the solid phase, these properties are explained using band theory. Band theory states: the atomic orbital of each atom overlap with the same orbital of their neighboring atoms in all directions to produce molecular orbital similar to those in small molecules.[1] When a sufficient amount of overlap occurs within a given range of energies, this results in continuous-like energy bands. If the band gap is small, these materials will then possess electrical properties (e.g. electrical conduction) similar to metals. The relative energies and number of electrons these bands possess depend upon the original atomic orbital (relative energy of highest occupied (valence band)) and lowest unoccupied band (conduction band) is known as the band gap (Figure 1.1).

At room temperature, conduction is not allowed for those bands that are empty or completely filled. A conventional conductive material requires a band gap narrow enough to thermally excite electrons to move from the valence band to the conduction band. The material behaves as a semiconductor when this occurs. If the band gap is too large, the valence band electrons fail to migrate to the conduction band resulting in an insulator (Figure 1.1). An example of this would be a typical plastic.

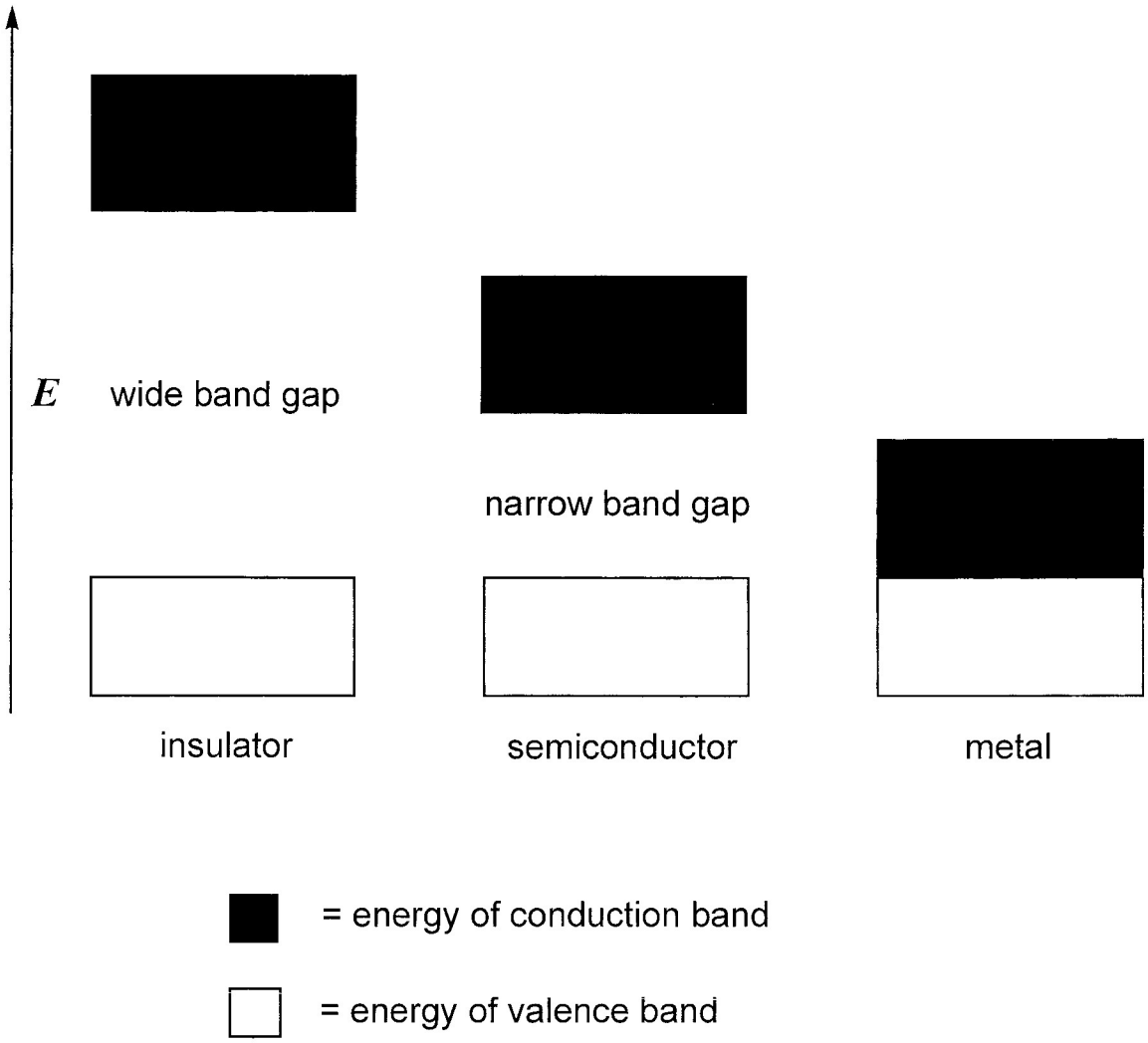


Figure 1.1. A molecular orbital illustration of an insulator, semiconductor, and conductor. [2]

Highly conductive metals that possess a zero band gap result in a full valence band and empty conduction band (metal) or partially full valence band and empty conduction band. Materials like this would include most metals (silver, copper, and iron).

Polymer Conduction. The mechanism for polymer conduction differs from conventional conductive materials. One difference includes: alternating single and double bonds (conjugated double bonds) required for conduction. Another difference is that a polymer does not need to have partially filled or partially empty bands. As a result, their electrical conductivity cannot be explained by simple band theory. Introduction of charge carriers (usually electrons or holes) causes conduction. Charge carriers are formed by doping, i.e., oxidation (p-type) or reduction (n-type) reaction, of the polymer chain. Oxidation, or p-type polymer charge carriers, leave a vacancy that does not delocalize completely. This vacancy is a hole or a radical cation that partially delocalizes over several monomeric units resulting in structural deformality. Energy will be greater in the newly deformed structure than the undoped polymer. Different charge carriers will be generated depending upon the ground state of the polymer (Figure 1.2).[3] The radical cation has destabilized the bonding orbital that has higher energy than the valence band. The band gap is the only difference between the destabilized bonding orbitals and the valence band. A value of 1.5 eV has been arbitrarily decided as the cutoff for low-band-gap conducting polymers.[4]

A conductive polymer produces a soliton[5], or polaron[6], depending on the polymer's ground state configuration when a radical cation is generated.

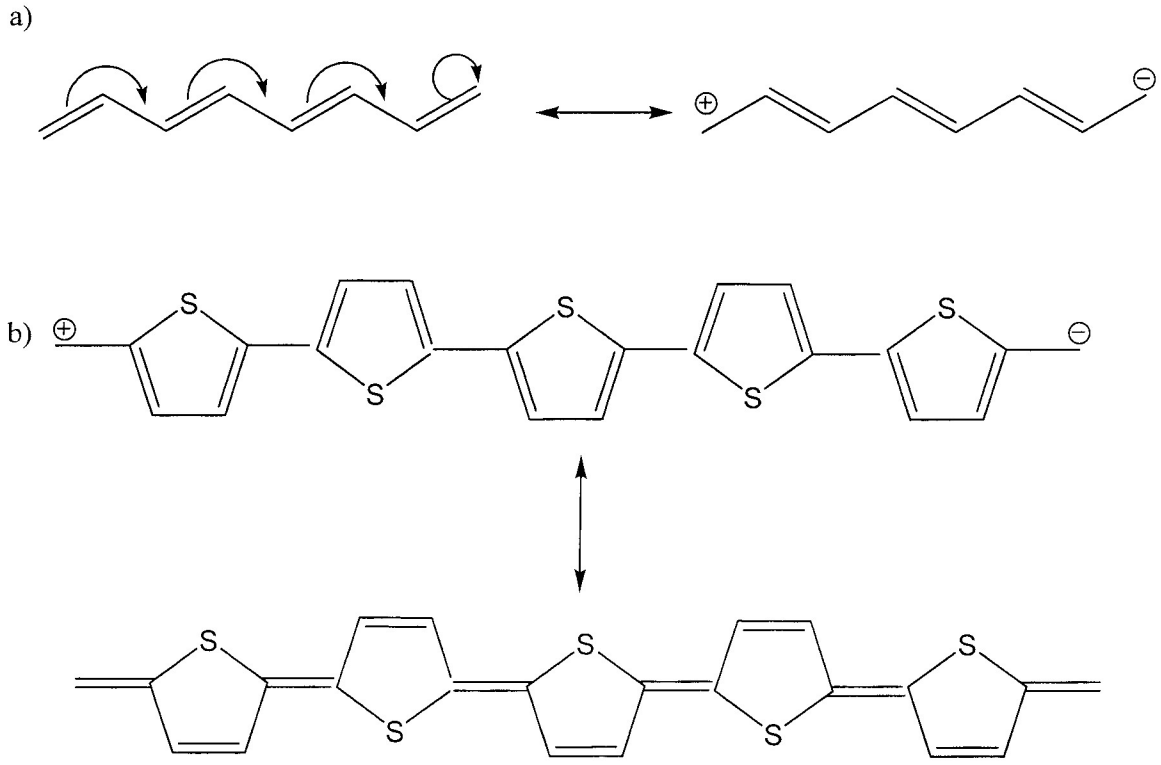


Figure 1.2. Examples of a (a) degenerate ground state configuration of polyacetylene and (b) nondegenerate ground sate configurations of polythiophene (top = aromatic form, bottom = quinoidal form).[2]

If the compound has a degenerate ground state (Figure 1.2), such as polyacetylene, the resulting radical cation will generate a soliton (Figure 1.3a). The positive charge and unpaired electron can move independently along the polymer chain (allowing for conduction) forming domains between the two identical parts of the bond alteration. However, a radical cation known as a polaron (Figure 1.3b) is generated by oxidation of a polymer with a nondegenerate ground state, such as polythiophene (Figure 1.2). The quinoidal form results from oxidation and is higher in energy than the ground state. The quinoidal form confines the charge and spin density to the localized structural deformation that is mobile along the chain. Two things can happen upon further oxidation of the nondegenerate polymer. One, a second electron can be removed from another segment of the polymer chain (resulting in a new polaron) or the unpaired electron from the previously formed polaron is removed. The latter produces a spinless state known as a bipolaron (Figure 1.3b). Conduction by polarons and bipolarons is generally considered to be the dominant mechanism of conductive polymers (Figure 1.4).

Conductive Polymer Background. Plastics or polymers are thought to behave oppositely from metals. Ideally, polymers behave as insulators while metals conduct electricity. Shirakawa and coworkers discovered conductive polymers in 1977.[6] These conductor polymers have been extensively studied, discovering that charge transfer oxidative doping of polyacteylene could increase its conductivity by 12 orders of magnitude.

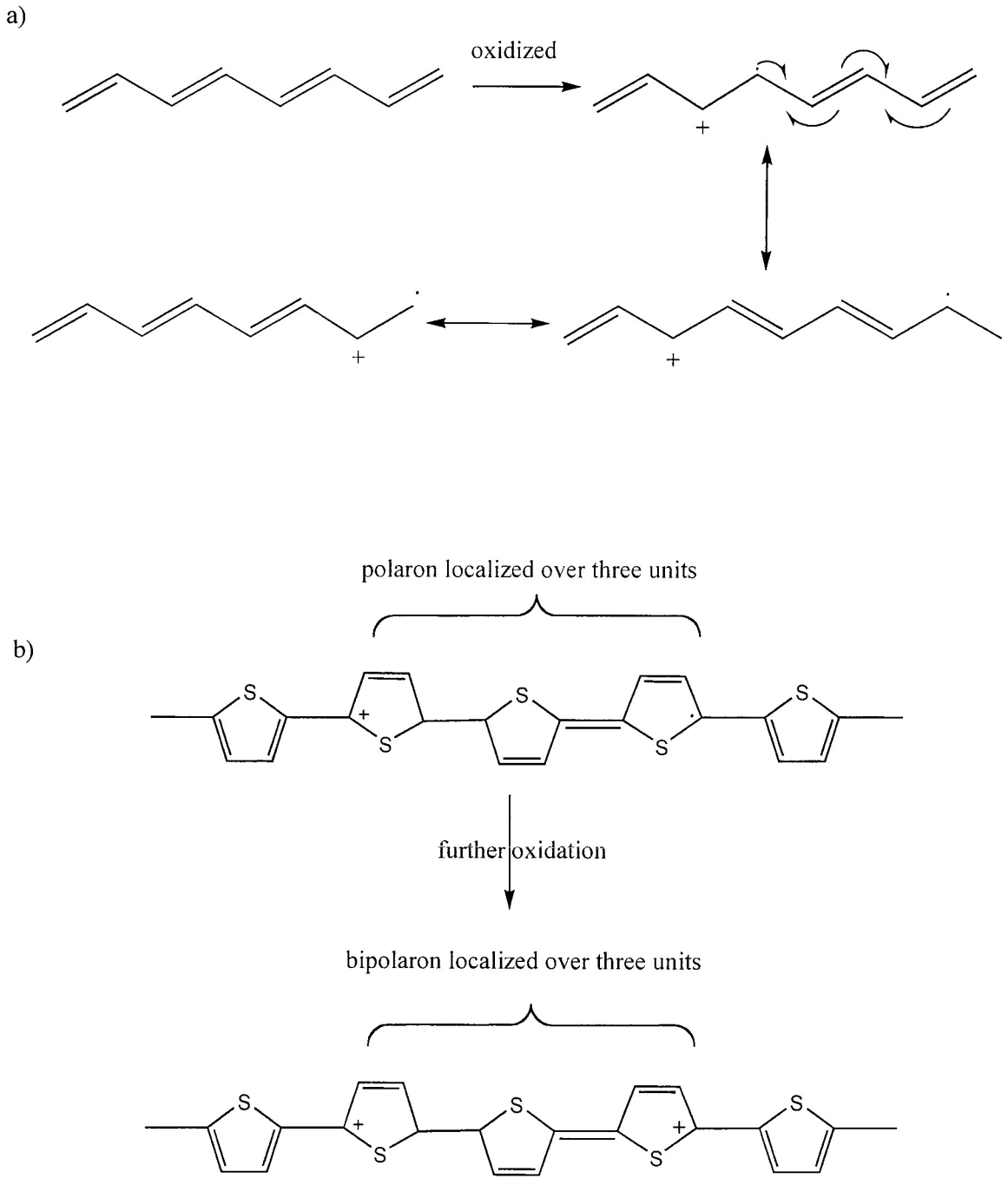


Figure 1.3. Representation of (a) soliton of polyacetylene and (b) polaron and bipolaron of polythiophene.[2]

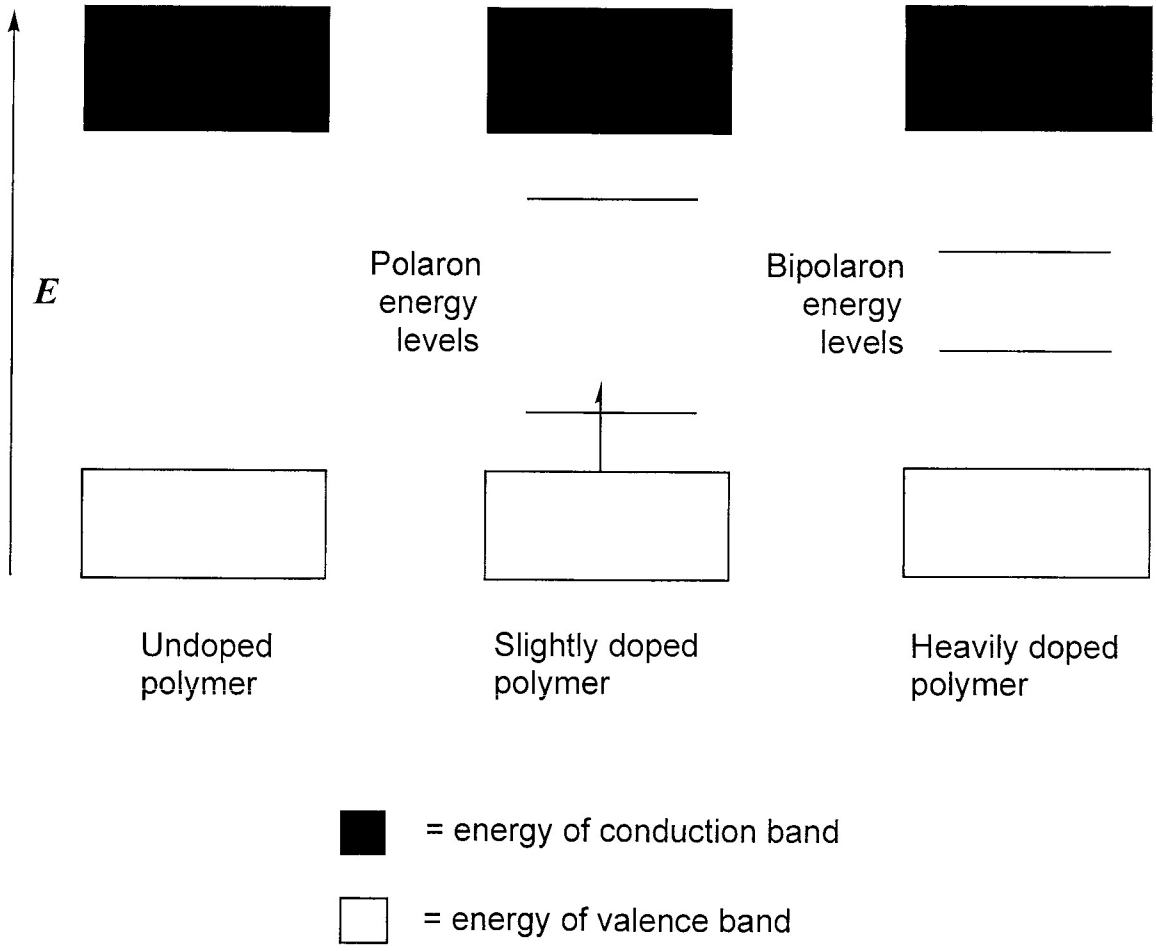


Figure 1.4. Relative energies of polaron and bipolaron levels.[2]

Other groups have envisioned a new class of polymers since Shirakawa's work. This new class would have either a zero energy band gap (a single continuous band consisting of valence and conduction bands) or a small band gap.[7] Polymers possessing a single, continuous band of overlapping valence and conduction bands should conduct as well as metals without the need for doping polymers that have overlapping bands display high electrical conductivity.[1] Polyacetylene is only conductive if oxidized with chlorine, bromine, or iodine vapor. Polyacetylene, by itself, is not conductive (10^{-15} – 10^{-14} S · m^{-1}) with a band gap of 1.50 – 1.7eV).[6,7] Upon doping, polyacetylene possesses a conductivity of 105 S · m^{-1}. For comparison, silver and copper have a conductivity of 108 S·m^{-1}.[6]

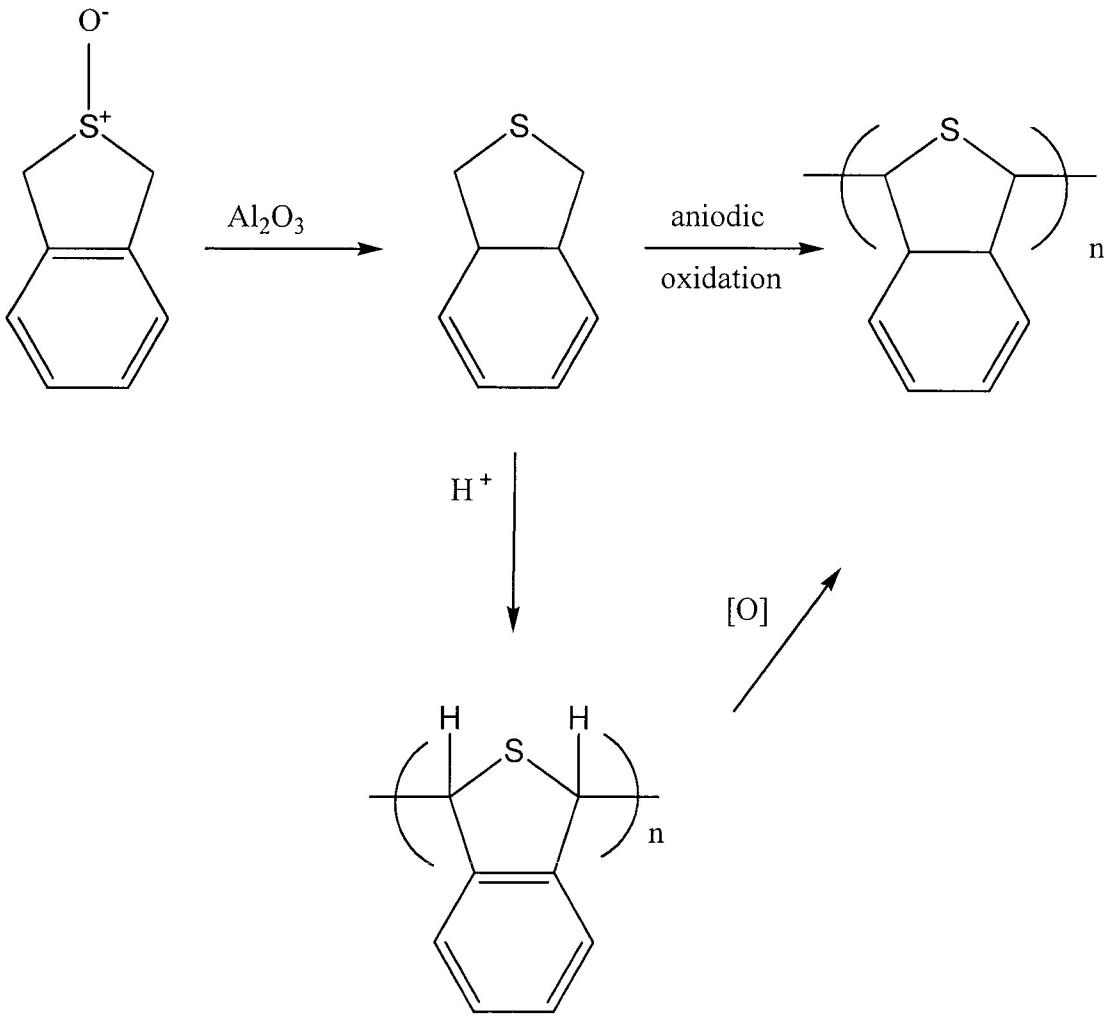
Polyacetylene, although showing promise as organic conductor, it is highly air-sensitive and oxidizes when exposed to molecular oxygen, therefore making this an unattractive use for commercial products. Attention has been focused on heterocylic aromatic polymers such as polythiophene and polypyrrole, in efforts to produce conductive polymers that are air-stable, tractable, and have a low band gap. The lone-pair electrons of the sulfur and nitrogen atoms tend to stabilize the positive charges of the p-doped polymers through resonance.[9]

One of the first low-band-gap heterocyclic aromatic polymers to be prepared was polyisothiananphthene (PITN) (also named [poly(benzo[*c*]thiophene)]).[9] In 1984, Wudl and Heeger synthesized PITN from its monomer (Scheme 1.1).[10] Cava and coworkers prepared benzo[*c*]thiophene by treatment of 1,3-dihydrobenzo[*c*]thiophene-2-oxide with Al_2O_3 at high temperature.[11] Using

LiBr in CH_3CN, electropolymerization of benzo[*c*]thiophene produced PITN as a blue-black, insoluble material in a nonconducting state. Chemical synthesis of PITN involved acid-catalyzed polymerization of benzo[*c*]thiophene producing polydihydroisothianphthene, which could be oxidized to PITN (Scheme 1.1). PITN conductivities have been reported ranging from 1-5000 $S \cdot m^{-1}$ depending upon preparation and doping. [12,13]

Polythiophene (PT) [14-18], polypyrrole (PP) [19-22] and their derivatives (Figure 1.5) are the most reported polymers owing to their synthetic ease and myriad applications. [23-26] PT and PP possess nondegenerate aromatic and quinoid states (Figure 1.2). It was stated by Bredas that as the contribution of the quinoid structure increases, the band gap decreases. [27] A source of new low-band-gap polymers would be provided by designing systems, such as, PT and PP.

There are other advantages offered by PTs such as environmental stability and structural versatility. When alkylated to poly(3-alkylthiophenes) (PATs), a significant improvement in conductivity is observed due to better ordering. Introduction of solubilizing groups is necessary to make highly conjugated organic materials solution processable. Typical nonconjugated solubilizing groups, however, reduce the density of the chromophores of the polymer. Frechet and coworkers[28] have developed a synthetic route that introduces a solubilizing group prior to polymerization, and then thermally removes it in the post-processing step.



Scheme 1.1. Synthesis of polyisothiananphthene. [9,10]

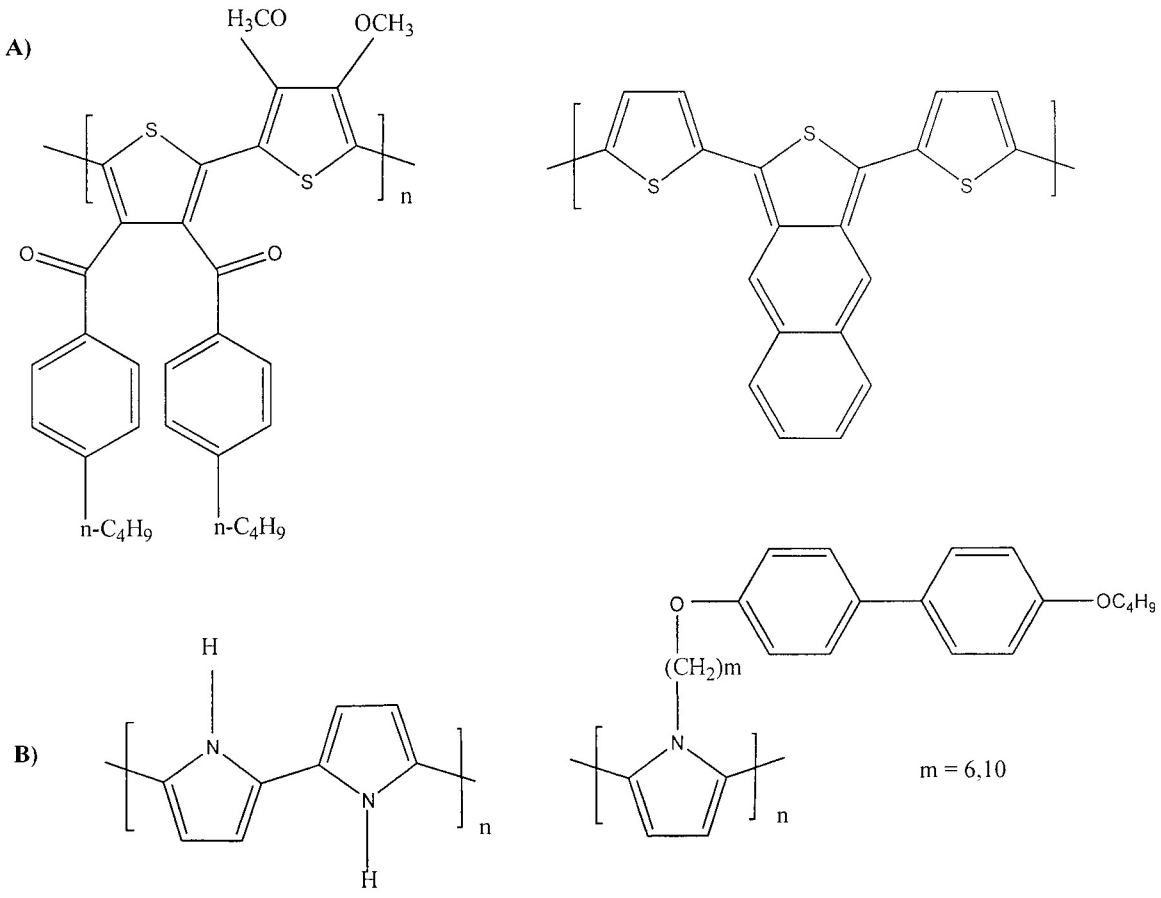


Figure 1.5. **A)** Polythiophene derivatives. [14,29] **B)** Polypyrrole[30,31] and a derivative.[21]

One can envision the field of conductive organic polymers to have grown from simple polythiophene to alkyl-substituted thiophenes to fused 5,6-membered thiophene derivatives. Our work focuses on a rarely investigated approach to the construction of polythiophene derivatives; in particular 5,5-fused systems known as cyclopenta[*c*]thiophenes.

II. SYNTHEIS AND CHARACTERIZATION OF 1,3-DISUBSTITUTED CYCLOPENTA[C]THIOPHENE: DIECKMANN CONDONSATION AND GRIGNARD ROUTE

Introduction

Skramstad first reported in 1969, the synthesis of 4*H*-cyclopenta[*c*]thiophene, also known as 2-thiapentalene (Figure 2.1.A) and its 1,3-dichloro derivative (Figure 2.1.B).[32] 2-Thiapentalene (Figure 2.1.A) was prepared in a 9-step synthesis in that report. Derivatives of 2-thiapentalene have also been reported in the literature. Wallace and Selegue[33] improved the synthesis of 1,3-dimethyl-4*H*-cyclopenta[*c*]thiophene (**9**) in 1999 (Scheme 2.1), originally synthesized by Cantrell and Harrison (Scheme 2.2).[34] These compounds are of significant interest since they are derivatives of thiophene as well as having great potential as organometallic compounds. It has been well documented that the fused 5-membered ring attached to thiophene can bind to a redox active metal center.[33] Complexes like these can be further oxidized or reduced. Unfortunately synthesizing cylcopenta[*c*]thiophenes or their organometallic complexes require long and tedious steps that often end in low yields.[33]

Our desire is to investigate cyclopenta[*c*]thiophene synthesis that requires fewer synthetic steps as reported by Skramstad and Wallace and Selegue. The challenge is which step or steps can we bypass that can lead to our desired product in good yields and purity.

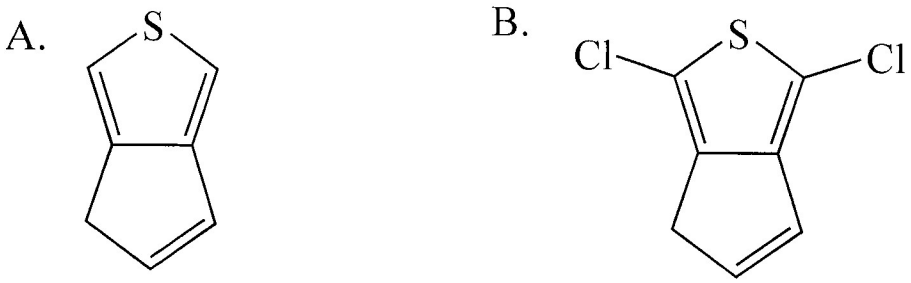
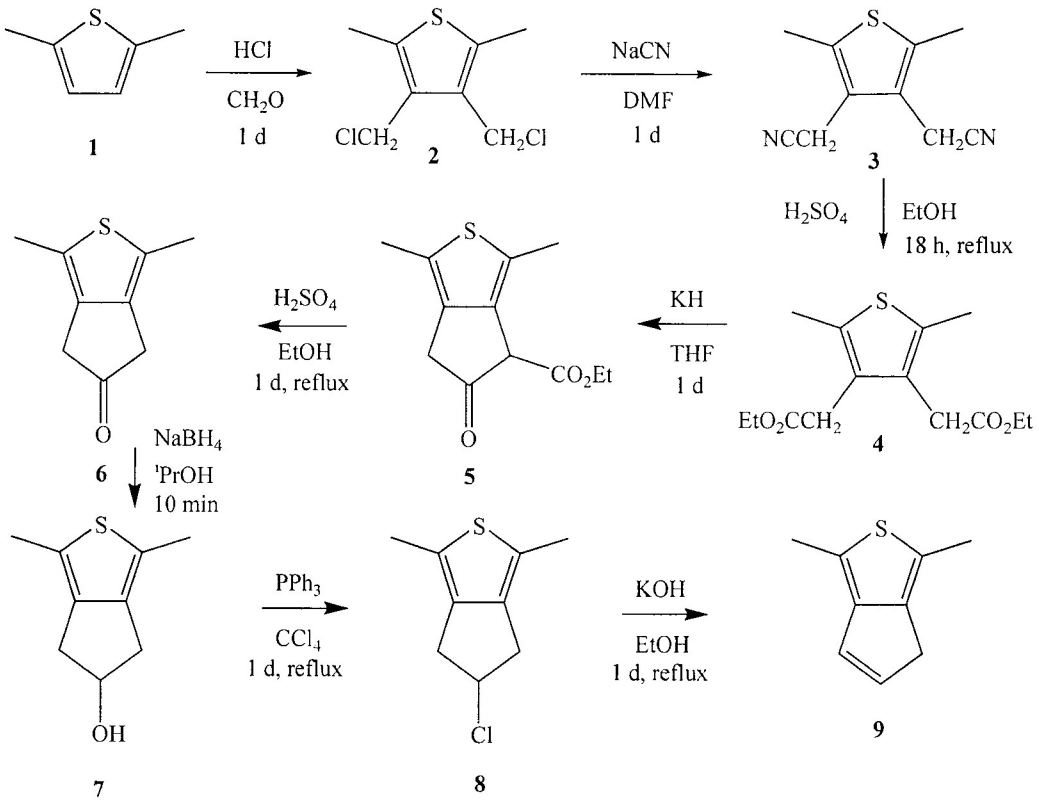
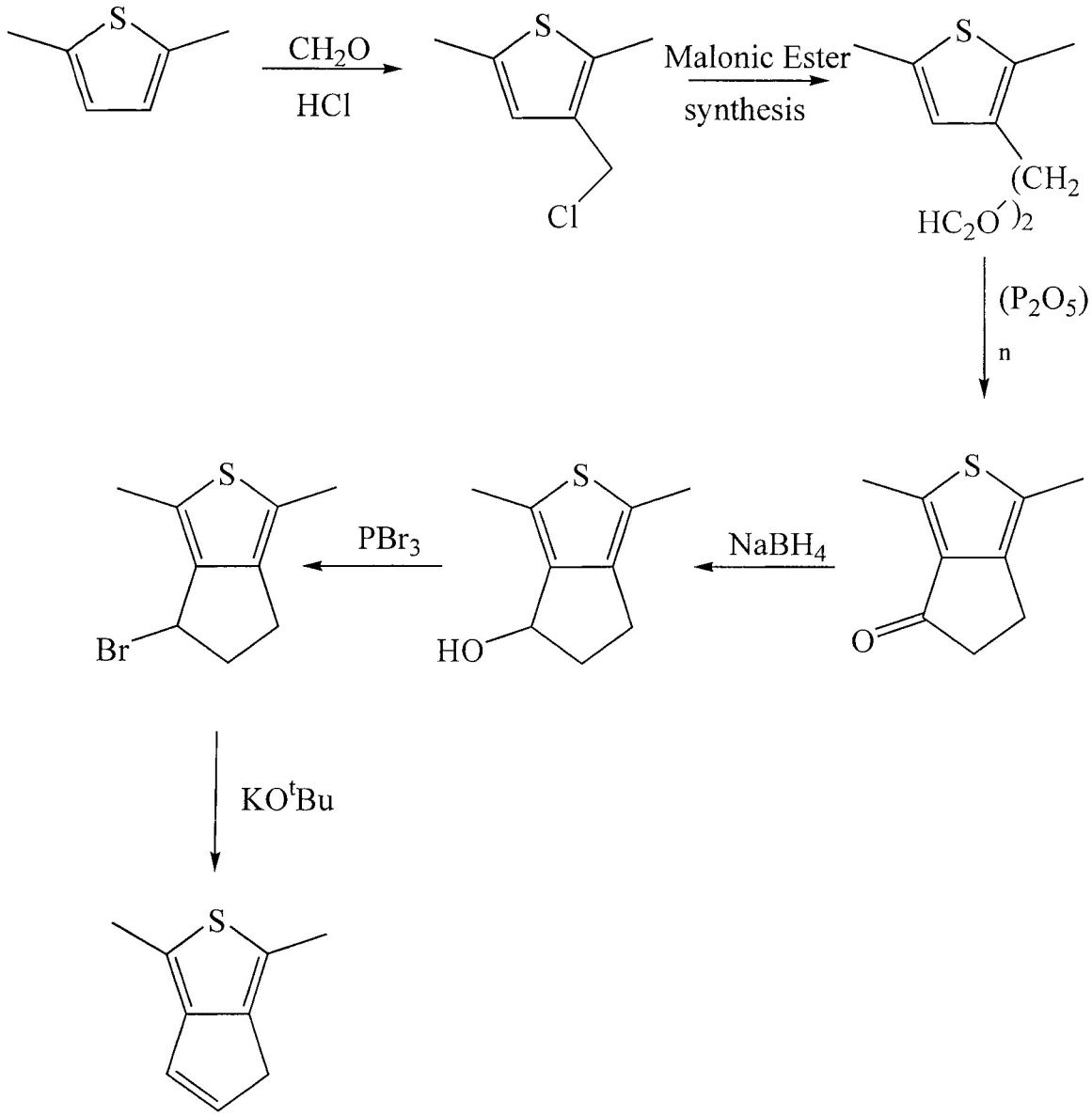


Figure 2.1. Structure of A. 2-thiapentalene and B. 1,3-dichloro-4*H*-cyclopenta[*c*]thiophene.[32]

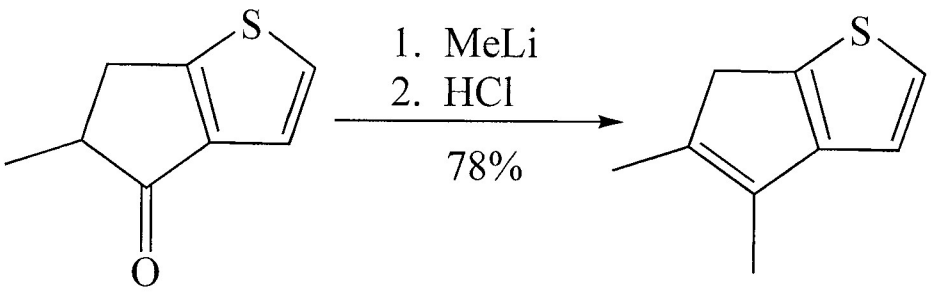


Scheme 2.1. Wallace and Selegue route for synthesis of thiapentalenes. [33]



Scheme 2.2. Cantrell and Harrison synthesis of 2,5-dimethylcyclopenta[*c*]thiophene.[34]

Our idea came from a paper published by Ryabov and coworkers where he treated 5-methyl-5,6-dihydro-4*H* cyclopenta[*b*]thiophene-1-one with a Grignard attack to eliminate to a cyclopenta[*b*]thiophene (Scheme 2.3).[35] Our modified route incorporated Wallace and Selegue's Dieckmann route (Scheme 2.4) up to ketone, 2,5-dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-5-one (**6**). In their route they synthesized 4,5-dimethyl-6*H*-cyclopenta[*c*]thiophene directly from a 5-methyl-5,6-dihydro-4*H*-cyclopenta[*b*]thiophene-1-one (Scheme 2.3). Using Ryabov's synthesis as a model, we took 1,3-dimethyl-4*H*-cyclopenta[*c*]thiophene (Scheme 2.4, **6**), and treated it with Ryabov's conditions to give 5-alkyl-1,3-dimethyl-4*H*-cyclopenta[*c*]thiophenes (Scheme 2.4, **7**). After ketone **6** (Scheme 2.4) was made, we then treated it with a Grignard reagent followed by an acidic workup to make the cylcopenta[*c*]thiophenes (Scheme 2.4). This particular reaction alone avoids a low yielding reduction step, found in Wallace and Selegue's route, as well as the toxic reagents utilized for the cholorosubstitution step.



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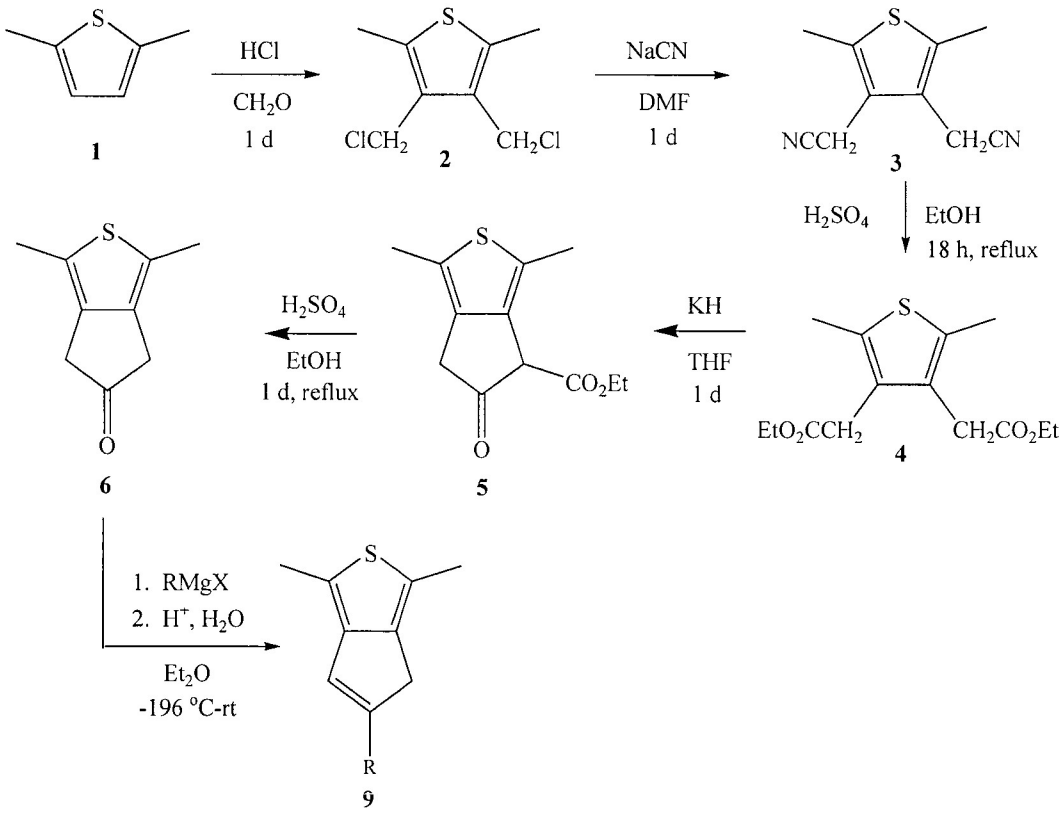
Scheme 2.3. Synthesis of 4,5-dimethyl-6*H*-cyclopenta[*b*]thiophene.[35]



Scheme 2.4. Synthesis of cyclopenta[*c*]thiophene by modified Dieckmann route.

III. EXPERIMENTAL PROCEDURES

Reactions were carried out by using standard organic synthetic techniques under air unless otherwise noted. $CDCl_3$ (Cambridge Isotopes) were used without further purification. 2,5-Dimethylthiophene (**1**), 3,4-Bis(chloromethyl)-2,5-dimethylthiophene (**2**), 3,4-Bis(cyanomethyl)-2,5-dimethlythiophene (**3**), 3,4-Bis-carboethoxy-2,5-dimethylthiophene (**4**), 1,3-Dimethyl-5-hydroxy-6-carboethoxy-4*H*-cyclopenta[*c*]thiophene (**5**), and 1,3-Dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-5-one (**6**) were prepared according to literature methods with our reported modifications (Scheme 2.1).[33] Aqueous formaldehyde (Eastman Chemicals), P_4S_{10} (Acros), KH (Aldrich), MeMgBr (Aldrich), and EtMgBr (Aldrich) were used without further purification. Diethyl ether was dried over sodium benzophenone ketyl.

^1H and ^{13}C NMR spectra were recorded on a JOEL-500MHz spectrometer at ca. 22°C and were referenced to residual solvent peaks. All ^{13}C NMR spectra listed were decoupled. Infrared spectra were recorded on a PerkinElmer Spectrum One FT-IR Spectrometer. Electron ionization (EI) mass spectra were recorded at 70 eV on a Varian Saturn GC/MS. Melting points were taken on a standard MEL-TEMP II apparatus.

Preparation of 2,5–Dimethylthiophene, $Me_2C_4H_2S$. (1)

2,5-Dimethylthiophene (Scheme **1**, 2.1) was previously synthesized by Jean and Nord.[36] An improvement of their synthesis is reported here. A 250 ml Erlenmeyer flask was charged with P_4S_{10} (24.4 g, 0.133 mol). 2,5-Hexanedione (38.0 g, 0.333 mol) was added drop-wise by a pastuer pipette. After addition, the mixture was stirred at room temperature overnight. The mixture turned dark brown. After decanting and distillation (135 °C), a clear, colorless liquid was obtained (21.5 g, 0.244 mol, 73.0%). **^{1}H NMR (500 MHz, $CDCl_3$, ppm):** δ2.45 (s, 6H, Me), 6.51 (s, 2H, C*H*). **^{1}H NMR (200 MHz, $CDCl_3$, ppm)**: δ2.44 (s, 6H, Me), 6.55(s, 2H, C*H*).[33] **^{13}C NMR (125 MHz, $CDCl_3$, ppm):** δ15.4 (*C*H_3), 124.9, 137.6 (Ar).

Preparation of 3,4-Bis-(chloromethyl)-2,5-dimethylthiophene, $(Me)_2C_4S(CH_2Cl)_2$. (2)

3,4-Bis-(chloromethyl)-2,5-dimethylthiophene was previously synthesized by Wallace and Selegue. [33] Details of a modification of their procedure are reported here. 2,5-Dimethylthiophene (10.0 g, 89.0 mmol) was added to a solution consisting of concentrated HCl (100 mL) and 36.8% aqueous formaldehyde solution (27.4 mL, 36 mmol). The solution, which was stirred at room temperature overnight, turned bright blue-green with a dark green solid precipitation out. Dichloromethane (200 mL) was added to dissolve the dark green solid. After separating the organic layer from the aqueous layer, the aqueous layer was extracted with another 100 mL of dichloromethane. The combined organic layers were dried by ($MgSO_4$). The organic solution was

eluted through a silica plug using 50:50 dichloromethane/hexane to give a clear solution. The volatiles were removed by rotary evaporation resulting in a white solid (**2,** scheme 2.1) (17.4 g, 83.2 mmol, 93.0%). **^{1}H NMR (500 MHz, $CDCl_3$, ppm):** δ2.40 (s, 6H, Me), 4.75 (s, 4H, C*H*$_2$). **^{1}H NMR (200 MHz, $CDCl_3$, ppm)[33]:** δ2.38 (s, 6H, Me), 4.59 (s, 4H, C*H*$_2$). **^{13}C NMR (125 MHz, $CDCl_3$, ppm):** δ12.9 (*C*H$_3$), 37.4 (*C*H$_2$), 132.1, 136.1 (Ar).

Preparation of 3, 4-Bis-(cyanomethyl)-2, 5-dimethylthiophene, $Me_2C_4S(CH_2CN)_2$. (3)

3,4-Bis-(cyanomethyl)-2,5-dimethylthiophene (**3**, Scheme 2.1) was previously synthesized by Helmers. [37] DMF (50 mL) was added to 3,4-bis-(chloromethyl)-2,5-dimethylthiophene (11.0 g, 52.7 mmol) and NaCN (5.68 g, 116 mmol) in a 250 mL round-bottom flask. The solution was stirred overnight at room temperature. Water (50 mL) was added to precipitate out the product. The pale yellow solid was filtered on a frit to remove most of the water then dissolved in dichloromethane. Water was removed from the organic solution by using a separatory funnel followed by drying agent ($MgSO_4$) giving a semicrystalline, yellow solid in the same amounts as previously reported (8.9 g, 50 mmol, 95%). **^{1}H NMR (500 MHz, $CDCl_3$, ppm):** δ2.45 (s, 6H, Me), 4.67 (s, 4H, CH_2). **^{1}H NMR (200 MHz, $CDCl_3$, ppm)[33]:** δ2.38 (s, 6H, Me), 4.59 (s, 4H, C*H*$_2$). **^{13}C NMR (125 MHz, $CDCl_3$, ppm):** δ12.1 (*C*H$_3$), 15.3 (*C*H$_2$), 116.0 (*C*N), 122.1, 133.9 (Ar).

Preparation of 3, 4-Bis-carboethoxy-2, 5-dimethylthiophene.

$Me_2C_4S(CH_2Cl)_2$. (4)

3,4-Bis-carboethoxy-2,5-dimethylthiophene (**4**, Scheme 2.1) was previously synthesized by Helmers.[37] Details of a modification of their procedure are reported here. Ethanol (250 mL) was added to 3,4-bis-(cyanomethyl)-2,5-dimethylthiophene (8.91 g, 50.0 mmol). The solution was cooled in an ice bath, and concentrated sulfuric acid (40 mL) was added slowly. The solution turned dark green/black upon addition of the acid. The solution was refluxed and monitored by periodic analysis of aliquots by GC/MS. After 48 hours, the reaction was complete. Water (500 mL) was added. The solution was extracted with CH_2Cl_2, dried ($MgSO_4$), and the volatiles were removed by rotary evaporation. Extraction of the material with pentane removed some of the unwanted amide produced in the reaction. The pentane was removed, and yellow-orange oil was distilled off from the resulting material at 135°/0.1 torr as a viscous semi-solid (10.9g, 38.4 mol, 76.6%) which was shown by GC-MS analysis to be pure diester. **^{1}H NMR (500 MHz, $CDCl_3$, ppm):** δ1.25 (t, 3H, J = 7.45 Hz, CH_2CH_3), 2.32 (s, 6H, Me), 3.54 (s, 4H, CH_2), 4.10 (q, 4H, J = 7.45 Hz, CH_2CH_3). **^{1}H NMR (200 MHz, $CDCl_3$, ppm):** [38] δ1.20 (m, 6H, CH_2CH_3), 2.31 (m, 6H, Me), 3.50 (m, 4H, CH_2), 4.95 (q, 4H, CH_2CH_3). **^{1}H NMR (200 MHz, $CDCl_3$, ppm):**[33] δ 1.2 (t, 6H), 2.3 (s, 6H), 3.5 (s, 4H), 4.1 (q, 4H). **^{13}C NMR (125 MHz, $CDCl_3$, ppm):** δ13.4 (thiophene-CH_3), 14.3 (OCH_2CH_3), 33.1 (CH_2CO), 60.9 (CH_2O), 129.4, 132.3 (thiophene), 171.1 (CO). GCMS: 284 *m/z* (M^+).

Preparation of 1,3-Dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-5-one, $Me_2SC_4CH_2(O)CH_2$. (6)

1,3-Dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-5-one (**6**, Scheme 2.1) was previously synthesized by Helmers.[37] Details of a modified procedure are reported here. 1,3-Dimethyl-5-hydroxy-6-carboethoxy-4*H*-cyclopenta[*c*]thiophene (**6**, 0.15 g, 0.90 mmol) was placed in 20% aqueous sulfuric acid solution (100 mL). The solution was refluxed overnight. After cooling the solution to room temperature, the solution was extracted with CH_2Cl_2 (100 mL). The organic layer was washed with more water (100 mL) and dried by ($MgSO_4$). The volatiles were removed by rotary evaporation to give the product as a dark brown solid in a quantitative yield. The ketone was eluted through a silica plug using 50:50 dichloromethane/hexane. The volatiles were removed by rotarty evaporation to give a light brown solid in quantitative yield. **^{1}H NMR (500 MHz, $CDCl_3$, ppm):** δ2.45 (s, 6H, Me), 3.27 (s, 4H, C*H*$_2$). **^{1}H NMR (200 MHz, CDCl3, ppm)[33]:** δ2.31 (s, 6*H*, Me), 3.25 (s, 4H, C*H*$_2$). **^{13}C NMR (125 MHz, $CDCl_3$, ppm):** δ13.6 (*C*H$_3$), 41.0 (*C*H$_2$), 128.3, 135.3 (Ar), 220.2 (*C*O).

Synthesis and Attempted Isolation of the 5-methyl-1,3-dimethyl-4*H*-cyclopenta[*c*]thiophenes (R = methyl, ethyl). (7)

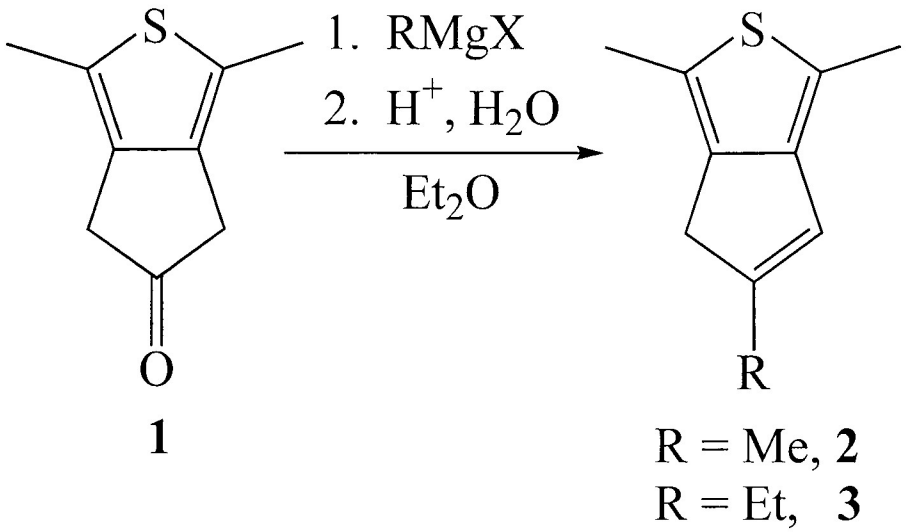
To a solution of 1,3-dimethyl-5,6-dihydro-4*H*-cylcppenta[*c*]thiophene-5-one (0.100 g, 0.602 mmol) in ether (10 mL) was added dropwise RMgBr (1.20 mmol) at 77 K. The mixture was stirred at room temperature for 1.5 h, then, 10 mL of 40% HCl was added dropwise at –10 °C. The resulting mixture was stirred for 40 min at room temperature. The organic layer was separated and the aqueous

layer was extracted with ether (3 x 15 mL), dried ($MgSO_4$), and reduced to an amber oil by rotary evaporation. Numerous attempts to purify cyclopenta[*c*]thiophenes by chromatography failed. Products appeared to decompose over 1–2 days. Evidence of their synthesis were observed in their ^{1}H and ^{13}C NMR spectra.

III. EXPERIMENTAL PROCEDURES

Reactions were carried out by using standard organic synthetic techniques under air unless otherwise noted. $CDCl_3$ (Cambridge Isotopes) were used without further purification. 2,5-Dimethylthiophene (**1**), 3,4-Bis(chloromethyl)-2,5-dimethylthiophene (**2**), 3,4-Bis(cyanomethyl)-2,5-dimethlythiophene (**3**), 3,4-Bis-carboethoxy-2,5-dimethylthiophene (**4**), 1,3-Dimethyl-5-hydroxy-6-carboethoxy-4*H*-cyclopenta[*c*]thiophene (**5**), and 1,3-Dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-5-one (**6**) were prepared according to literature methods with our reported modifications (Scheme 2.1).[33] Aqueous formaldehyde (Eastman Chemicals), P_4S_{10} (Acros), KH (Aldrich), MeMgBr (Aldrich), and EtMgBr (Aldrich) were used without further purification. Diethyl ether was dried over sodium benzophenone ketyl.

^1H and ^{13}C NMR spectra were recorded on a JOEL-500MHz spectrometer at ca. 22°C and were referenced to residual solvent peaks. All ^{13}C NMR spectra listed were decoupled. Infrared spectra were recorded on a PerkinElmer Spectrum One FT-IR Spectrometer. Electron ionization (EI) mass spectra were recorded at 70 eV on a Varian Saturn GC/MS. Melting points were taken on a standard MEL-TEMP II apparatus.



Scheme 4.1 Synthesis of 5-alkyl-1,3-dimethyl-4*H*-cyclopenta[*c*]thiophenes.

route, but instead incorporate their route to provide a shorter synthetic procedure to get to cyclopenta[*c*]thiophenes. We have followed their synthetic procedure up to ketone formation, 1,3-dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-5-one (**1**, Scheme 4.1). After the ketone was made, we were able to reduce the number of steps to substitute cyclopenta[*c*]thiophene. Problems erupted along the way to the ketone (**1**, Scheme 4.1) when mimicking Wallace and Selegue's experimental procedures exactly. Here we report the necessary modifications that allowed us to obtain our ketone needed for the final step to cyclopenta[*c*]thiophene synthesis. Additional spectroscopy, not provided by Wallace and Selegue, are also provided for our cyclopenta[*c*]thiophene intermediates.

2,5-Dimethylthiophene was previously synthesized by Wallace using a 2 L 3-neck round-bottom flask fit with a mechanical stirrer, condenser, and a dropping funnel. We obtained similar results (70.0%) using a 250-mL Erlenmeyer flask set over ice while drop-wise adding 2,5-hexanedione to P_4S_{10} via pastuer pipette. Our attempt was as successful as Wallace's method without the need for large and more expensive glassware. After filtration we obtained 2,5-dimethylthiophene as a colorless liquid. This compound showed two singlets in its ^{1}H NMR spectrum at ~δ2.45 (C*H*$_3$) and δ6.51 (C*H*), respectively (Figure 4.1). The singlet observed at 2.45 ppm is typical for methyl chemical shifts for all 2,5-dimethylthiophene compounds. The singlet corresponding to the alkene (C*H* bond) found at 6.51 ppm is typical for thiophene C*H* signals. These chemical shifts are very similar to Wallace's reported values of 2.44 ppm (C*H*$_3$) and 6.55

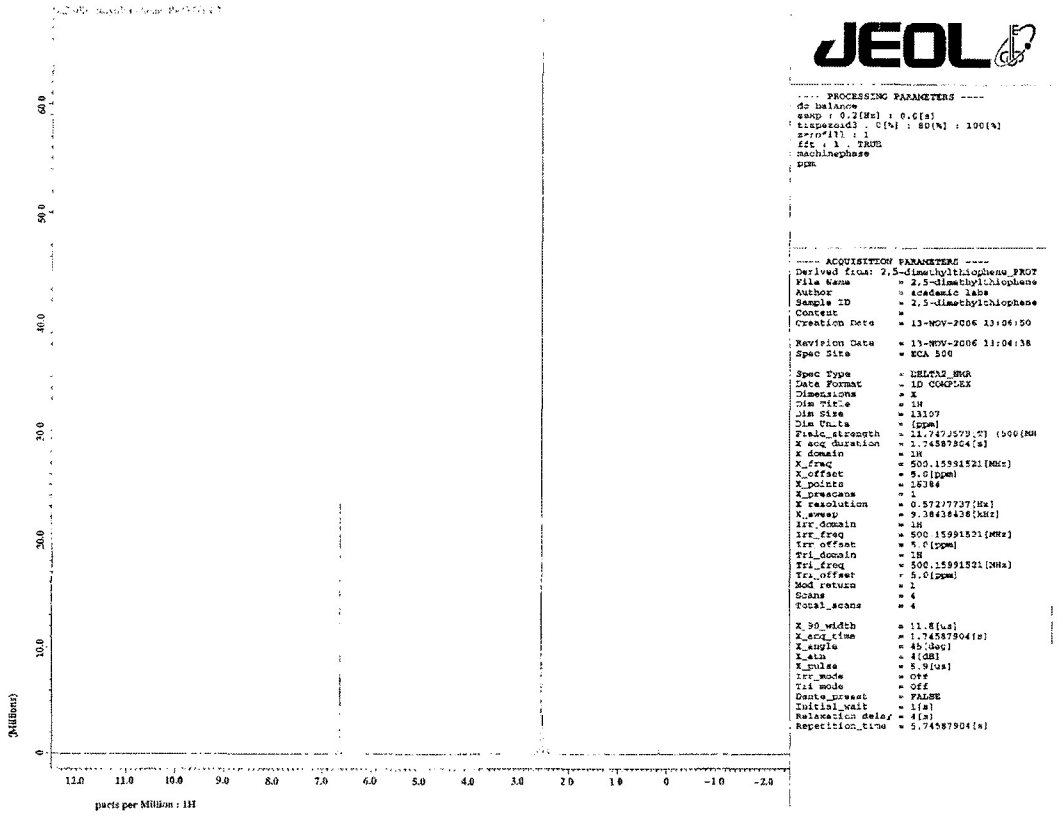


Figure 4.1 ^{1}H NMR structure for 2,5-Dimethylthiophene.

ppm (C*H*). 2,5-Dimethylthiophene showed its expected three signals in the ^{13}C NMR spectrum at ~ δ15.4 (CH_3), 124.9, and 137.6 (Ar) (Figure 4.2).

The singlet observed at 15.4 ppm is typical for methyl-substituted carbons attached to thiophene. The singlets corresponding to the thiophene ring carbons have values typically found in the 120-140 ppm range. Although Wallace and Selegue did not report ^{13}C NMR values for 2,5-dimethylthiophene, these values match closely with 2,5-dimethylthiophene derivatives found in the chemical literature.

Previous synthesis of 3,4-bis-(chloromethyl)-2,5-dimethylthiophene recorded by Wallace rarely gave a pale yellow solid. Instead the final product was a dark purple solid that required further purification not mentioned in his report. In order to obtain a pure product we eluted the dichloride through a silica plug with a 50/50 dichloromethane/hexane mixture. The volatiles were removed by rotary evaporation that gave a pearl white solid (85.0-90.0% yield). These yields were comparable to Wallace and Selegue's amounts however the purity was much greater. This compound showed two singlets in its ^{1}H NMR spectrum at ~δ2.40 (CH_3) and δ4.75 (CH_2), respectively (Figure 4.3). Our singlet observed at 2.40 ppm is similar to Wallace and Selegue's methyl chemical shifts reported at 2.38 ppm. The singlet corresponding to the methylene (CH_2) protons found at 4.75 ppm is also similar to the reported value of 4.59 ppm. It is interesting to note that the experimental methylene chemical shift (4.75 ppm) for our dichloride is very close to the theoretically calculate value of 4.61 ppm (Table 4.1). 3,4-Bis

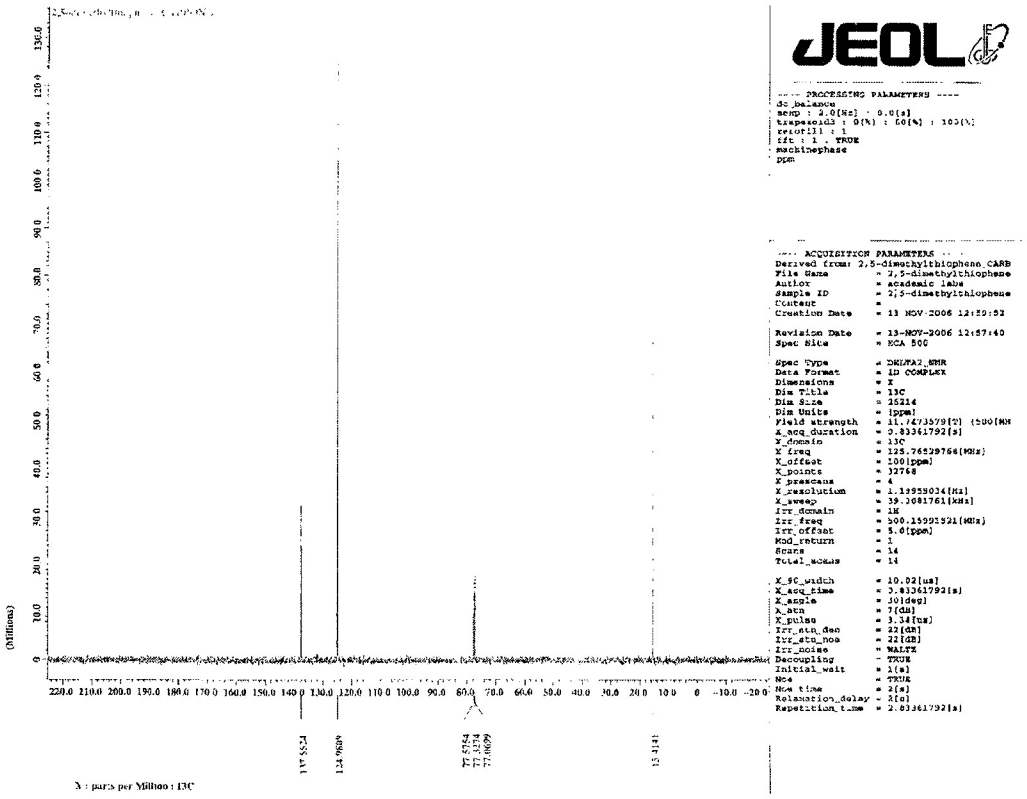


Figure 4.2. ^{13}C NMR structure for 2,5-Dimethylthiophene.

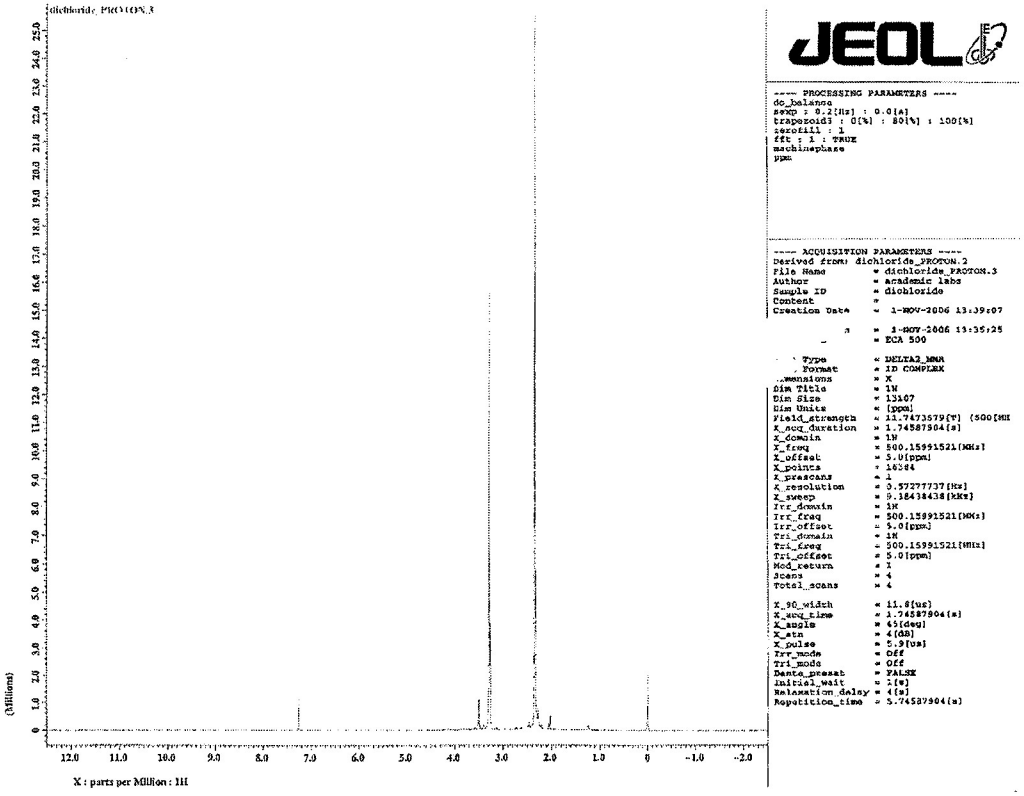
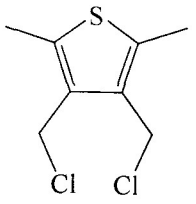
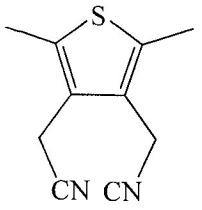
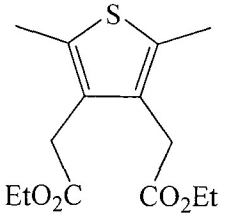
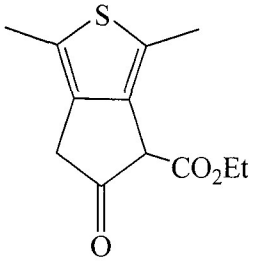
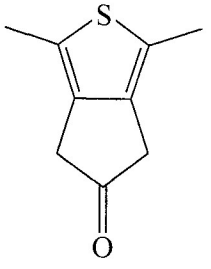


Figure 4.3 ^{1}H NMR structure for 3,4-Bis(chloromethyl)-2,5-dimethylthiophene.

Table 4.1 Theoretical and Experimental Methylene Chemical Shifts of Cyclopenta[*c*]thiophene Intermediates. Theoretical assignments based on Shoolery's Rule: δ (Y–CH_2–Z) = 0.23 + σY + σZ.

Compound	Theoretical Value (ppm)	Experimental Value (ppm)
	4.61	4.75
	3.65	4.67
	3.52	3.54
	3.56	3.2–3.5
	3.56	3.25

-(chloromethyl)-2,5-dimethylthiophene showed it's expected four signals in the ^{13}C NMR spectrum at ~ δ13.7 (CH_3), 41.0 (CH_2), 129.9, and 135.1 (Ar) (Figure 4.4). The signal observed at 13.7 ppm is typical for methyl-substituted carbons attached to thiophene. The methylene carbon chemical shift was found at 41.0 ppm, as expected. Again, the signals corresponding to the thiophene ring carbons have values typically found in the 120-140 ppm range. Wallace and Selegue did not report ^{13}C NMR values for 3,4-bis-(chloromethyl)-2,5-dimethylthiophene.

No improvements were needed for the synthesis of 3,4-bis-(cyanomethyl)-2,5-dimethylthiophene. Our yields were comparable to Wallace and Selegue's percent yield for the dinitrile (95%). This compound showed two singlets in its ^1H NMR spectrum at ~ δ2.45 (CH_3) and δ4.67 (CH_2), respectively (Figure 4.5). Our singlet observed at 2.45 ppm was similar to Wallace and Selegue's methyl chemical shifts reported at 2.37 ppm. However, our singlet corresponding to the methylene (CH_2) protons found at 4.67 ppm was observed to be further downfield than Wallace and Selegue's reported value of 3.60 ppm. The dinitrile's theoretical methylene chemical shift more closely matches that of Wallace and Selegue's value (3.51 ppm) as compared to our own (Table 4.1). 3,4-Bis-(cyanomethyl)-2,5-dimethylthiophene showed its expected five signals in the ^{13}C NMR spectrum at ~ δ12.1 (CH_3), 15.3 (CH_2), 116.0 (CN), 122.1, and 133.9 (Ar) (Figure 4.6). The signal observed at 12.1 ppm is typical for methyl-substituted carbons attached to thiophene. The methylene carbon, bound to a less electron-withdrawing group, such as CN, chemical shift was found further upfield (15.3 ppm), as expected when compared to 3,4-bis-(chloromethyl)-2,5-

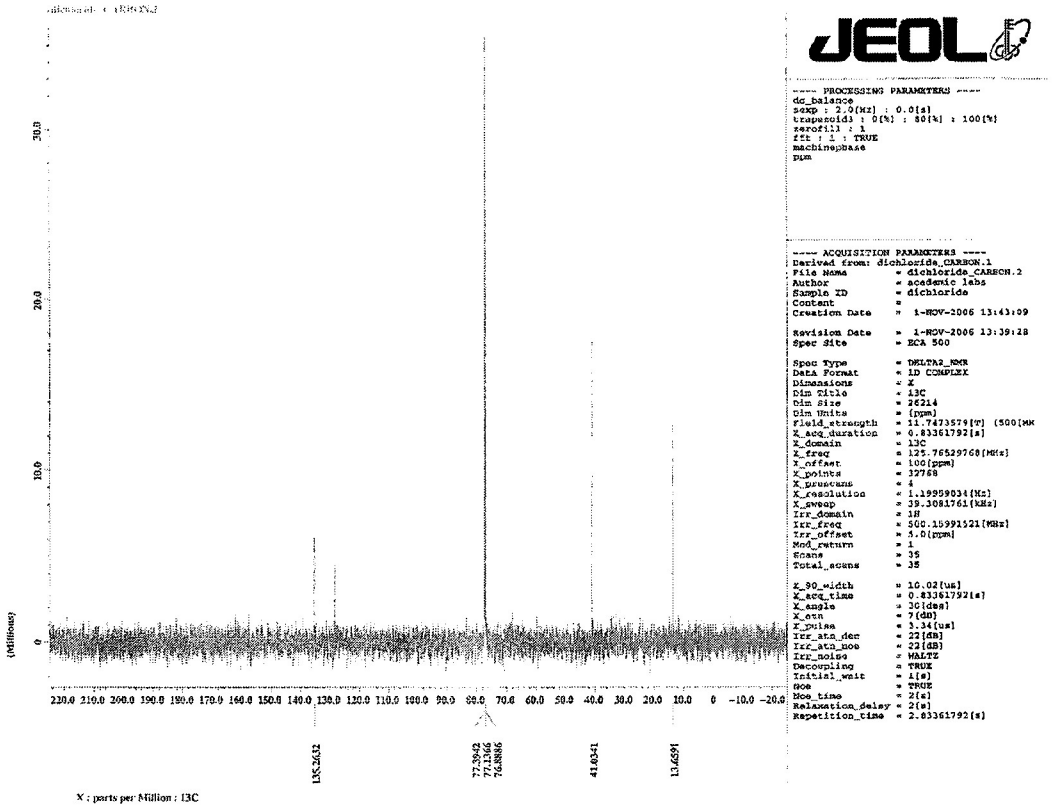


Figure 4.4. ^{13}C NMR structure for 3,4-Bis(chloromethyl)-2,5-dimethylthiophene.

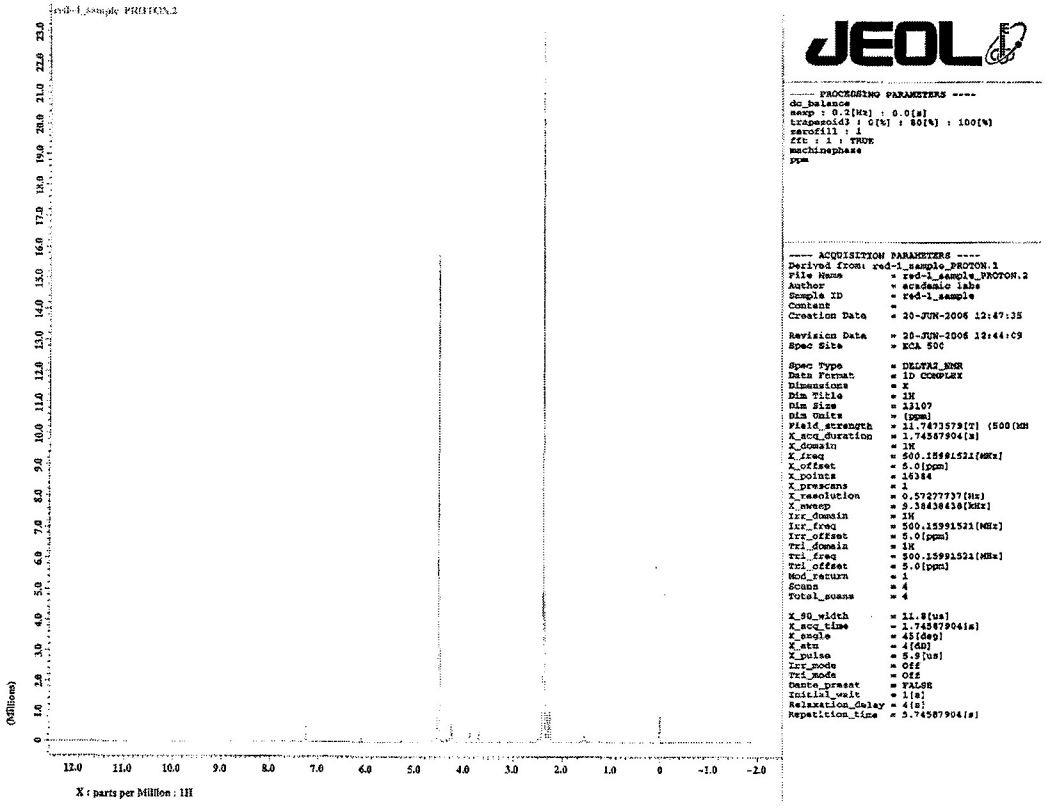


Figure 4.5 ^{1}H NMR structure for 3,4-Bis(cyanomethyl)-2,5-dimethylthiophene.

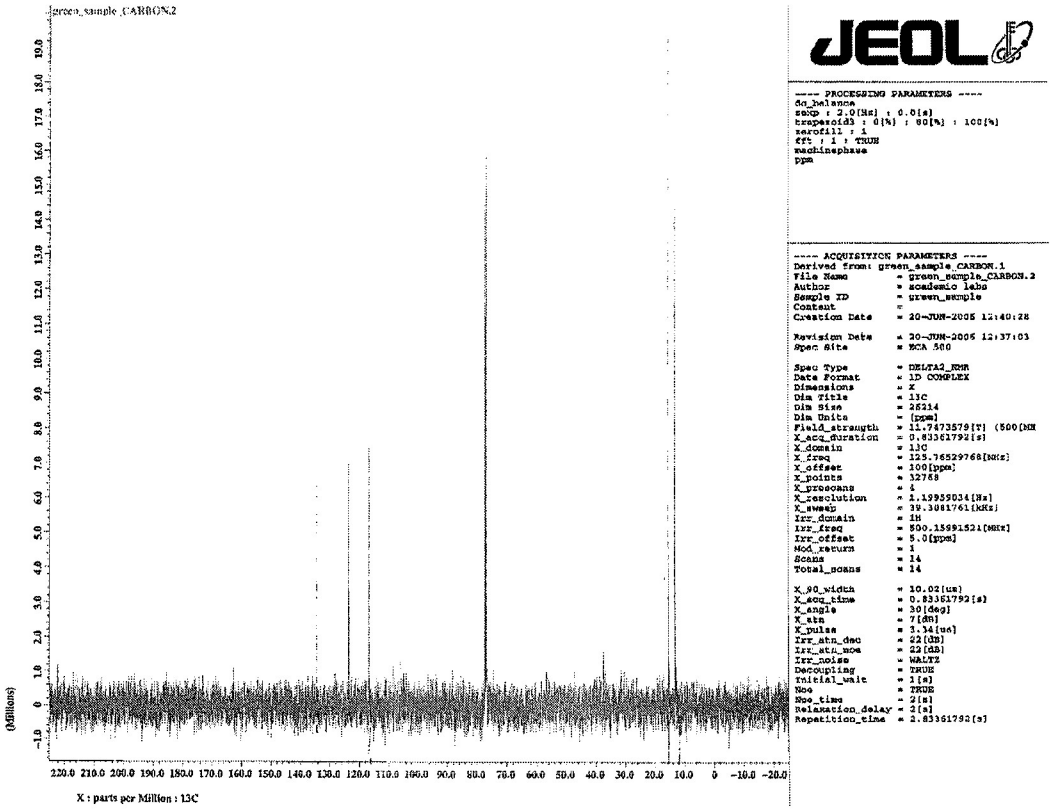


Figure 4.6 ^{13}C NMR structure for 3,4-Bis(cyanomethyl)-2,5-dimethylthiophene.

dimethylthiophene. Wallace and attached to thiophene. The methylene carbon chemical shift was found at 41.0 ppm, as expected. Again, the signals corresponding to the thiophene ring carbons have values typically found in the 120-140 ppm range. Wallace and Selegue did not report ^{13}C NMR values for 3,4-bis-(chloromethyl)-2,5-dimethylthiophene.

No improvements were needed for the synthesis of 3,4-bis-(cyanomethyl)-2,5-dimethylthiophene. Our yields were comparable to Wallace and Selegue's percent yield for the dinitrile (95%). This compound showed two singlets in its ^{1}H NMR spectrum at ~ δ2.45 (CH_3) and δ4.67 (CH_2), respectively (Figure 4.5). Our singlet observed at 2.45 ppm was similar to Wallace and Selegue's methyl chemical shifts reported at 2.37 ppm. However, our singlet corresponding to the methylene (CH_2) protons found at 4.67 ppm was observed to be further downfield than Wallace and Selegue's reported value of 3.60 ppm. The dinitrile's theoretical methylene chemical shift more closely matches that of Wallace and Selegue's value (3.51 ppm) as compared to our own (Table 4.1). 3,4-Bis-(cyanomethyl)-2,5-dimethylthiophene showed its expected five signals in the ^{13}C NMR spectrum at ~ δ12.1 (CH_3), 15.3 (CH_2), 116.0 (CN), 122.1, and 133.9 (Ar) (Figure 4.6). The signal observed at 12.1 ppm is typical for methyl-substituted carbons attached to thiophene. The methylene carbon, bound to a less electron-withdrawing group, such as CN, chemical shift was found further upfield (15.3 ppm), as expected when compared to 3,4-bis-(chloromethyl)-2,5-dimethylthiophene. Again, the signals corresponding to the thiophene ring carbons have values typically found in the 120-140 ppm range. Wallace and

Selegue did not report ^{13}C NMR values for 3,4-bis-(cyanomethyl)-2,5-dimethylthiophene.

There were a few modifications made to 3,4-bis-carboethoxy-2,5-dimethylthiophene synthesis. The first modification step required increased reflux time in concentrated H_2SO_4 (8 hours versus 48 hours) in order to transform our dinitrile to the desired diester. When refluxing for only 8 hours, as suggested by Wallace and Selegue, we obtained a mixture of diamide, amide-ester, and diester as observed by GCMS. However, when refluxing for 48 h, GCMS analysis showed complete conversion of dintrile to diester (M^+ = 284 *m/z*, Figure 4.7). Our second modification involved diester purification. We also noticed that following the pentane step in our workup distillation and column chromatography were not needed for further purification. Our ^1H NMR spectra matched that of Wallace and Selegue's reported values. However, Wallace and Selegue did not report a ^{13}C NMR analysis for the diester. Our ^{13}C NMR analysis of 3,4-bis-carboethoxy-2,5-dimethylthiophene showed its expected seven signals at ~ δ 13.4 (CH_3), 14.3 (CH_3), 33.1 (CH_2), 60.8 (OCH_2CH_3), 129.4, 132.3 (Ar), and 171.1 (*C*O) ppm (Figure 4.8). The signal observed at 12.1 ppm is typical for methyl-substituted carbons attached to thiophene. The methylene carbon, bound to a less electron-withdrawing group, such as CN, chemical shift was found further upfield (15.3 ppm), as expected when compared to 3,4-bis-(chloromethyl)-2,5-

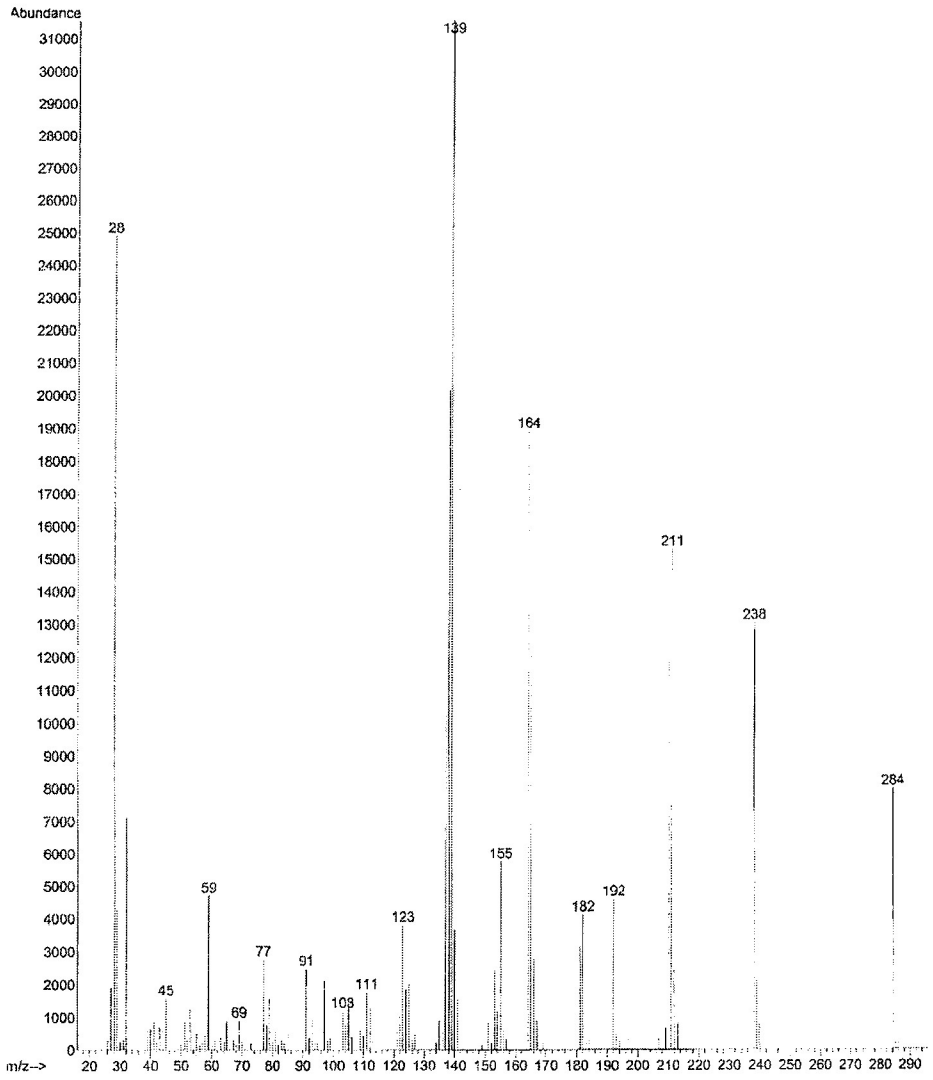


Figure 4.7 GCMS analysis of 3,4-Bis-carboethoxy-2,5-dimethylthiophene.

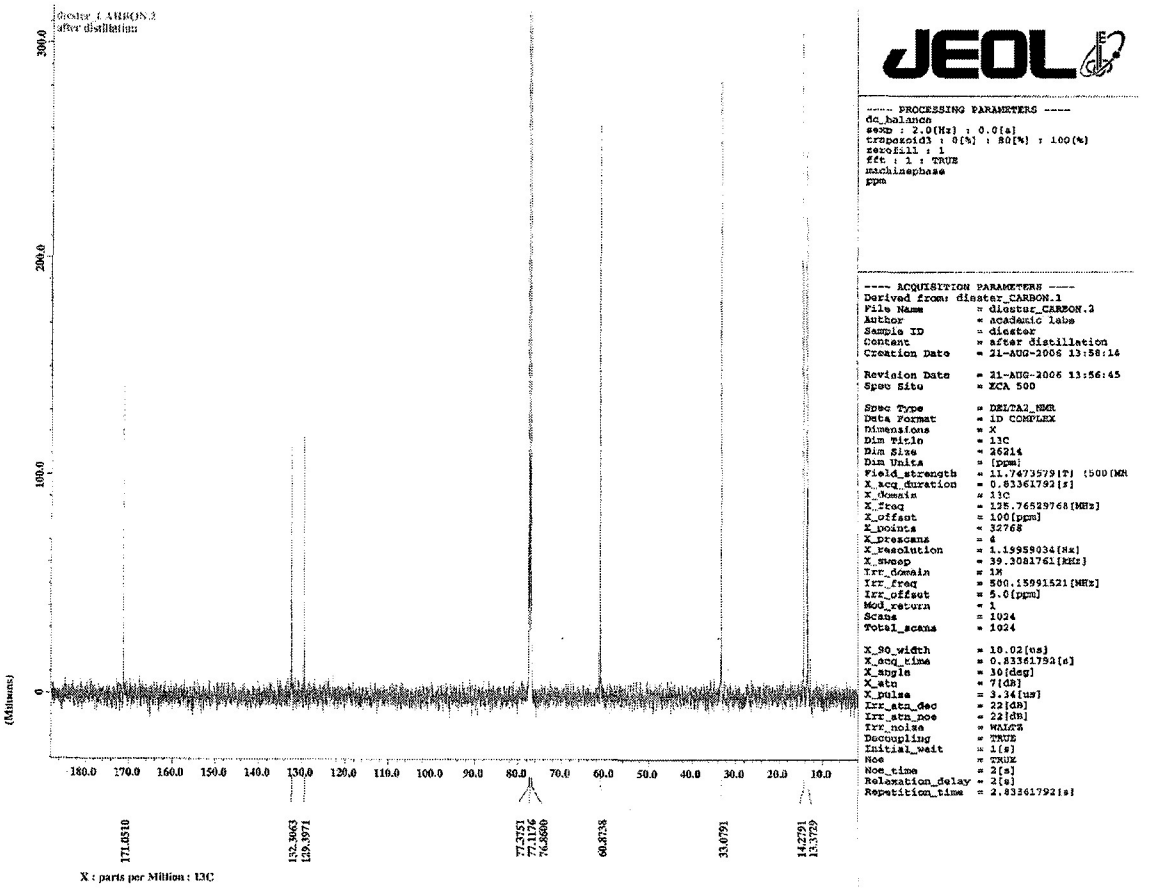


Figure 4.8 ^{13}C NMR structure for 3,4-Bis-carboethoxy-2,5-dimethylthiophene. dimethylthiophene.

Again, the signals corresponding to the thiophene ring carbons have values typically found in the 120-140 ppm range. Wallace and Selegue did not report ^{13}C NMR values for 3,4-bis-(cyanomethyl)-2,5-dimethylthiophene.

1,3-Dimethyl-5-hydroxy-6-carboethoxy-4*H*-cyclopenta[*c*]thiophene was generated as according to Wallace and Selegue's report. No further modifications were made.

1,3-Dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-5-one, previously recorded by Wallace and Selegue, gave a dark brown solid. In order to obtain a more pure product we eluted the ketone through a silica plug with a 50/50 dichloromethane/hexane mixture. This step eliminated some of the by-products. However, some contaminants remained. Several attempts to purify via column chromatography failed. Attempts to purify via recrystallization and sublimation also failed. We are certain that the purity of our product affected the next step in our reaction sequence; cyclopenta[*c*]thiophene synthesis and purification. Our percent yield was equivalent to that reported by Wallace and Selegue (quantitative yield). This compound showed two singlets in its ^{1}H NMR spectrum at ~δ2.31 (CH_3) and δ3.25 (CH_2), respectively (Figure 4.9). Our singlet observed at 2.31 ppm matched Wallace and Selegue's methyl chemical shift exactly. The singlet corresponding to the methylene (CH_2) protons found at 3.29 ppm was also similar to the reported value of 3.25 ppm. It is interesting to note that our ketone's

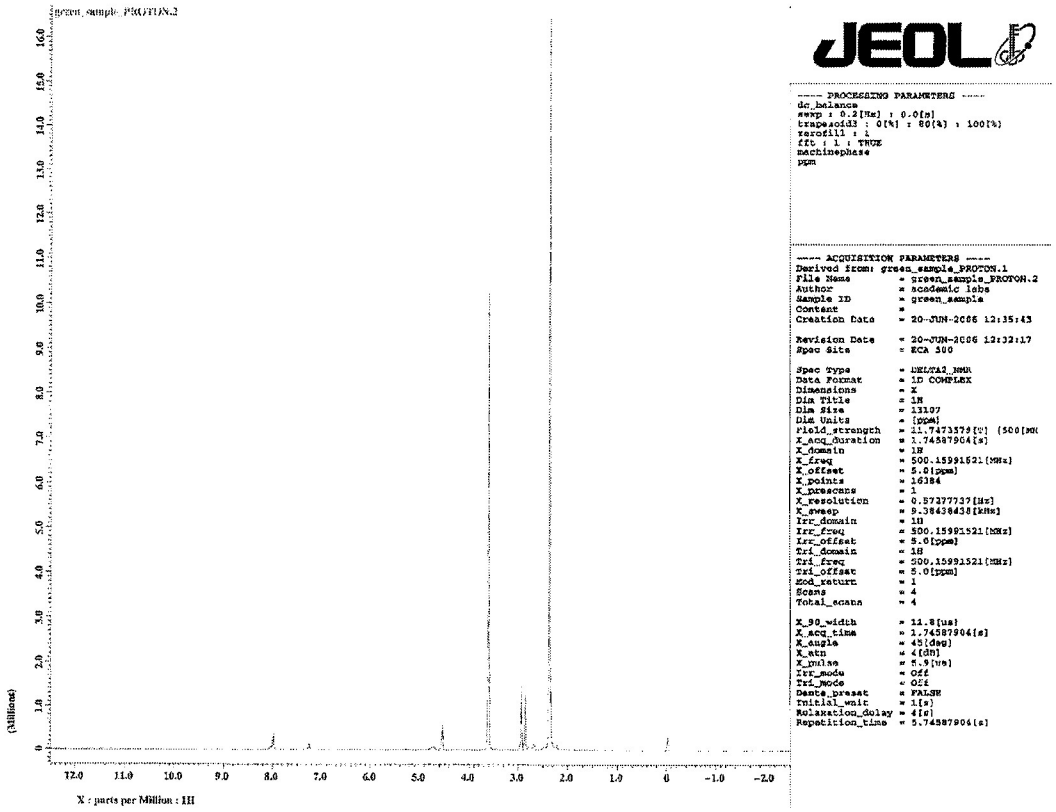


Figure 4.9 ^{1}H NMR structure for 1,3-Dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]-thiophene-5-one.

experimental methylene chemical shift (3.25 ppm) was very close to the theoretically calculated value (3.56 ppm, Table 4.1). 1,3-Dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-5-one showed its expected five signals in the ^{13}C NMR spectrum observed at ~ δ13.7 (CH_3), 41.0 (CH_2), 128.1, and 135.3 (Ar), and 216.1 (*C*O). The signal observed at 13.7 ppm is typical for methyl-substituted carbons attached to thiophene. The methylene carbon chemical shift was found at 41.0 ppm, as expected. Again, the signals corresponding to the thiophene ring carbons have values typically found in the 120-140 ppm range. Finally, the carbonyl carbon was found in its expected downfield region of 160–200+ ppm. Wallace and Selegue did not report ^{13}C NMR values for 1,3-dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-5-one.

Ketone **1** (Scheme 4.1) was obtained according to previously reported methods.[7] Compound **1** was then treated with an alkyl (R = Me, Et) Grignard reagent in dry ether, similar to those conditions employed by Ryabov and coworkers[9] (Scheme 2.3) to obtain 4,5-dimethyl-6*H*-cyclopenta[*b*]thiophene. Treating ketone **1** (Scheme 4.1) with an alkylmagnesium bromide followed by acidic workup afforded the 5-alkyl-1,3-dimethyl-4*H*-cyclopenta[*c*]thiophenes, 5-methyl-1,3-dimethyl-4*H*-cyclopenta[*c*]thiophenes (**2**) and 5-ethyl-1,3-dimethyl-4*H*-cyclopenta[*c*]thiophenes (**3**), in good yield (60.0% and 65.0%, respectively) as amber oils. Analytical purity could not be obtained due to the instability of these compounds.

^{1}H and ^{13}C NMR analysis of compounds **2** and **3** (Scheme 4.1) display the thiophene methyl groups as two singlets at 2.3–2.4 ppm as expected. As with 1,3-

dimethyl-4*H*-cyclopenta[*c*]thiophene, the methylene protons are observed as singlets (3.0–3.1 ppm). The 5-methyl protons for **2** were observed as a singlet (1.51 ppm, 3H), and **3** displayed a triplet (1.5 ppm, ^{3}J = 7 Hz, 3H) and quartet (1.8 ppm, ^{3}J = 7 Hz, 2H) corresponding to the ethyl group. The alkene protons for compounds **2** and **3** were observed as singlets at 5.10 and 5.12 ppm, respectively. In the ^{13}C NMR spectra, the vinyl and thiophene carbon resonances for **2** and **3** are observed between 120-140 ppm, typical for thiapentalenes reported.[10,11] Attempts to obtain an analytically pure sample of compounds **2** and **3** (Scheme 4.1) were unsuccessful as they readily decompose in air within minutes.

In conclusion, alkyl Grignard attack of **1** afforded thiapentalenes **2** and **3**. The presence of the 5-alkyl substituted thiapentalenes were shown by ^{1}H and ^{13}C NMR. Future research will continue to focus on the synthesis and purification of these substituted cyclopenta[*c*]thiophenes as well as investigating their incorporation into organometallic complexes.

V. CONCLUSIONS

The work presented in this thesis was to synthesize substituted cyclopenta[*c*]thiophenes from 2,5-dimethylthiophene in fewer steps than the current Dieckmann synthesis route reported by Wallace and Selegue. These cyclopenta[*c*]thiophenes were synthesized as potential semiconductors. Unfortunately, the best reported route to making cyclopenta[*c*]thiophenes had several omissions for their experimentals. We filled the necessary gaps to obtain each cyclopenta[*c*]thiophene intermediately. We previously synthesized 2,5-dimethylthiophene by using smaller and less expensive pieces of glassware than those reported by Wallace and Selegue. This synthesis led to the formation of 3,4-bis-(chloromethyl)-2,5-dimethylthiophene upon treating with HCl and aqueous formaldehyde. This compound required further purification than previously reported by Wallace and Selegue. We twice eluted the dichloride through a silica plug followed by rotary evaporation to obtain a much greater purity for our dichloride. For the reaction of 3,4-bis-(cyanomethyl)-2,5-dimethylthiophene, no improvement was required. Our percent yields were very similar to Wallace and Selegue's amount (quantitative). The diester required much more work to obtain the purity previously reported. 3,4-Bis-carboethoxy-2,5-dimethylthiophene synthesis required a dramatically increased reflux time in concentrated H_2SO_4 to transform the dinitrile to the diester. The diester we made then had to be further purified via vacuum distillation. 1,3-Dimethyl-5-hydroxy-6-carboethoxy-4*H*-cyclopenta[*c*]thiophene was then synthesized from 3,4-Bis-carboethoxy-2,5-dimethylthiophene without any additional modifications

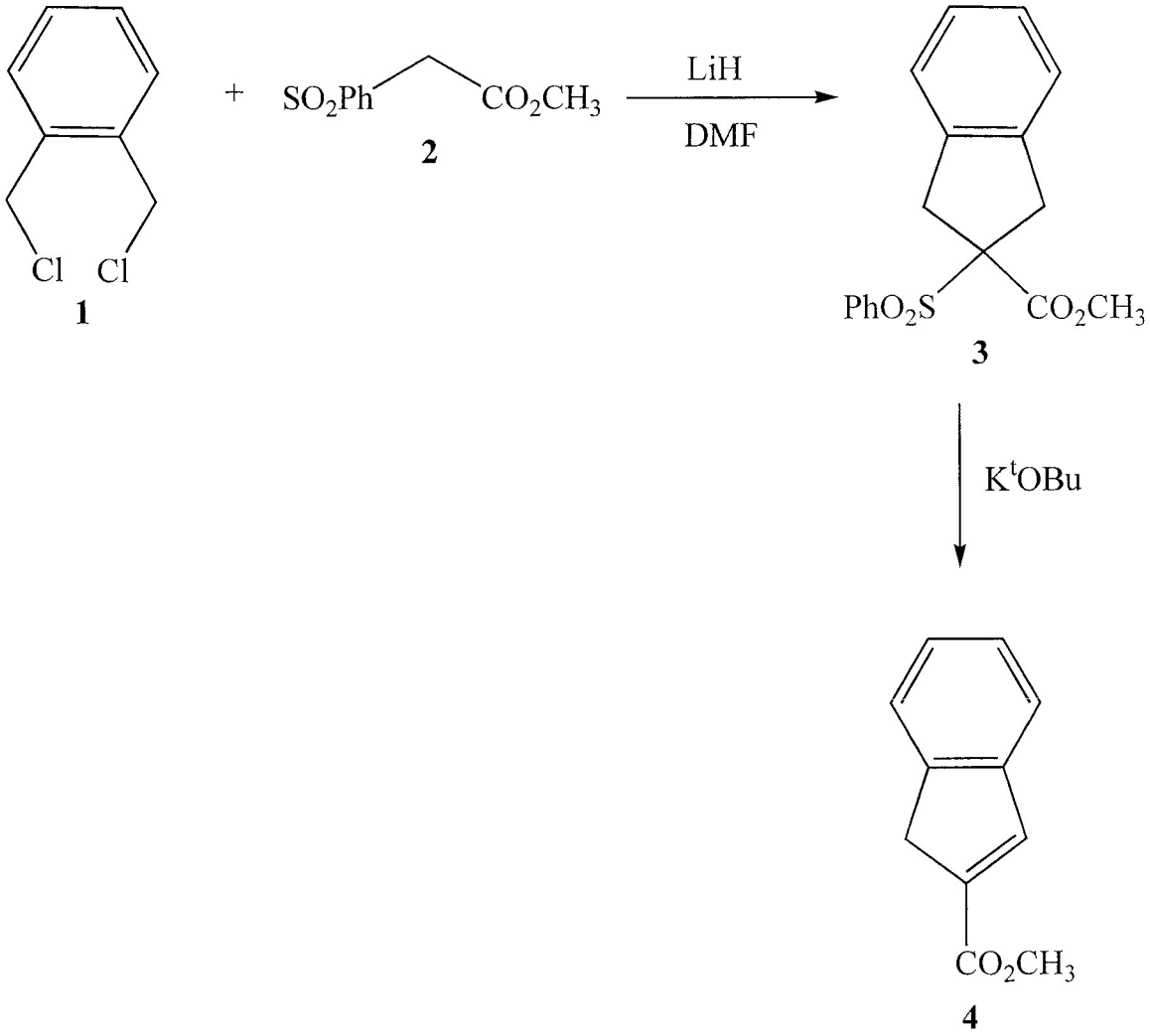
required. 1,3-Dimethyl-5-hydroxy-6-carboethoxy-4*H*-cyclopenta[*c*]thiophene is not made readily, this 5,5-fused membered ring system is very difficult to make because it is very strained. 1,3-Dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-5-one was synthesized from 1,3-Dimethyl-5-hydroxy-6-carboethoxy-4*H*-cyclopenta[*c*]thiophene. In order to form a more pure product than reported, we eluted this compound through a silica plug which did not eliminate all contaminants. We attempted other purification techniques but were not successful. Our ketone compound was then treated with an alkyl (Me and Et) Grignard reagent resulting in good yields. However, the yields cannot be taken with confidence since isolation and purification wasn't successful due to the time remaining.

VI. CONTINUING RESEARCH

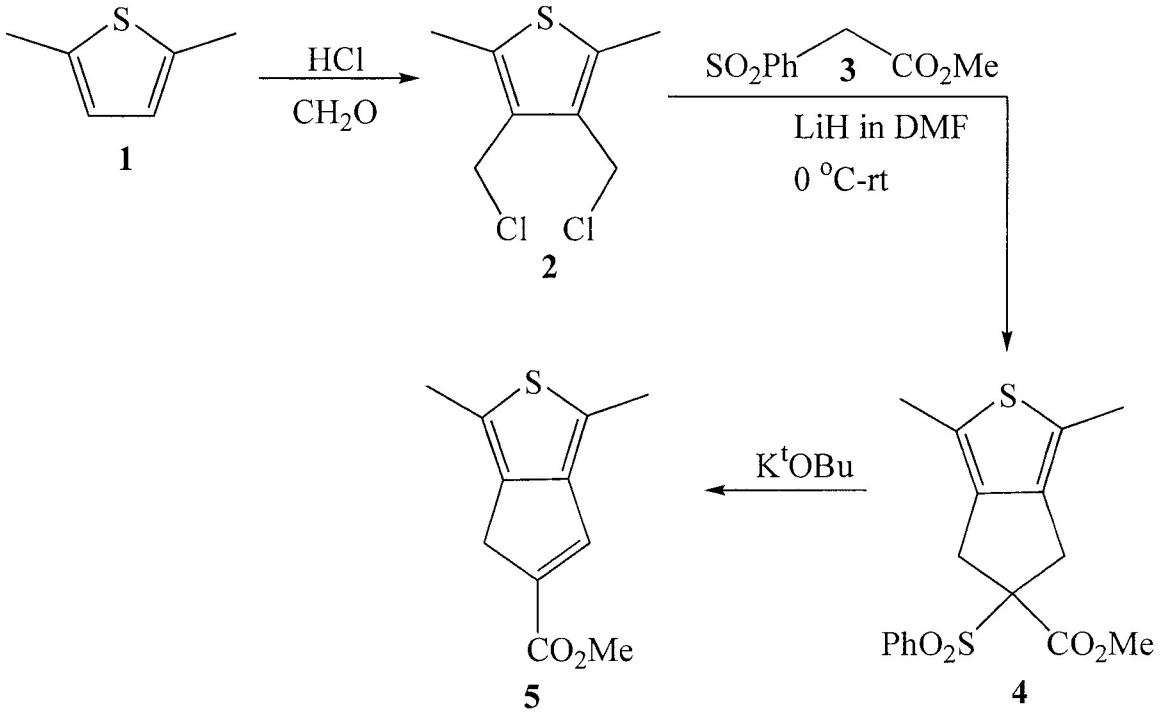
The next step in this project is to purify, and fully characterize, the 5-alkyl-1,3-dimethyl-4*H*-cyclopenta[*c*]thiophenes (alkyl = Me, Et) that were produced from reacting 1,3-dimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]-thiophene-5-one with an appropriate Grignard followed by an elimination step. Fortunately, we were able to characterize (using ^{1}H and ^{13}C NMR spectroscopy) each intermediate generated in the modified Wallace and Selegue route that was utilized in our research goal. Also, we were able to fill in all necessary experimental conditions that were omitted in several of Wallace and Selegue's reports. Unfortunately, due to time remaining we were not able to obtain the purification conditions that would allow for isolation and full characterization of these 5-alkyl-1,3-dimethyl-4*H*-cyclopenta[*c*]thiophenes. Obtaining the correct purification conditions would be a good start for the next graduate student.

In future research, our dichloride (3,4-bis(chloromethyl-2,5-dimethythiophene)) could be converted to substituted cyclopenta[*c*]thiophenes in much fewer synthetic steps with a lot less work. Our 6-step synthesis is too long for these compounds. Contamination is still a very real issue and is preventing full final product characterization. If we were to reduce the number of synthetic steps even more we should be able to arrive to our final product with less contamination and in greater yields. We believe that if given enough time on our project, our dichloride could be directly converted to a 5,5'-sulfone ester that would eliminate to a cyclopenta[*c*]thiophene. Our idea for this originated from the research conducted by Palandoken and coworkers. They performed a two step

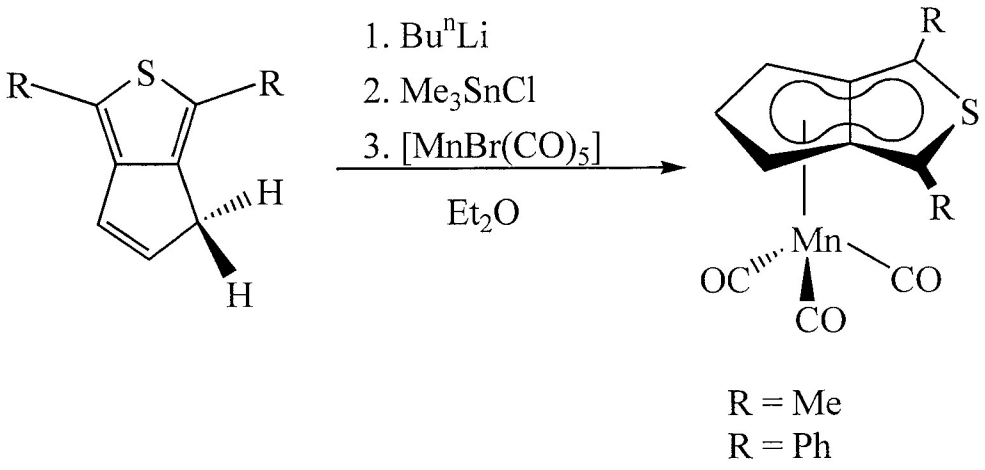
reaction for indene (**4**, Scheme 6.1.) synthesis by treating an activated methylene (methyl phenylsulfonylacetate, **2**, Scheme 6.1.) with a dichloride (α,α-dichloro-*o*-xylene, **1**, Scheme 5.1.). Their dichloride **1** is structurally and chemically similar to our dichloride **2** (Scheme 6.2.) and should make the desired sulfone ester (**5**, Scheme 6.2.) as well. By using Palandoken and coworkers strategy as a model for our cyclopenta[*c*]thiophene synthesis, the ultimate goal is a three step synthesis using activated methylene (Scheme 6.2.). This shorter synthetic route would provide desired cyclopenta[*c*]thiophenes in reduced time, provide less contamination, and avoid some hazardous and toxic chemicals (NaCN). Ultimately these compounds will be converted into organometallic cyclopenta[*c*]thienyl metal complexes (Scheme 6.3). The results of this project could be done in one or two more semesters.



Scheme 6.1. 2-(Hydroxymethyl)indene synthesis from dichloride **1**.



Scheme 6.2. 3-Step route to substituted cyclopenta[*c*]thiophene beginning with 2,5-dimethylthiophene.



Scheme 6.3. Cyclopenta[*c*]thienyl metal complexes from cyclopenta[*c*]thiophenes.

VII. REFERENCES

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Publications resulting from thesis research:

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